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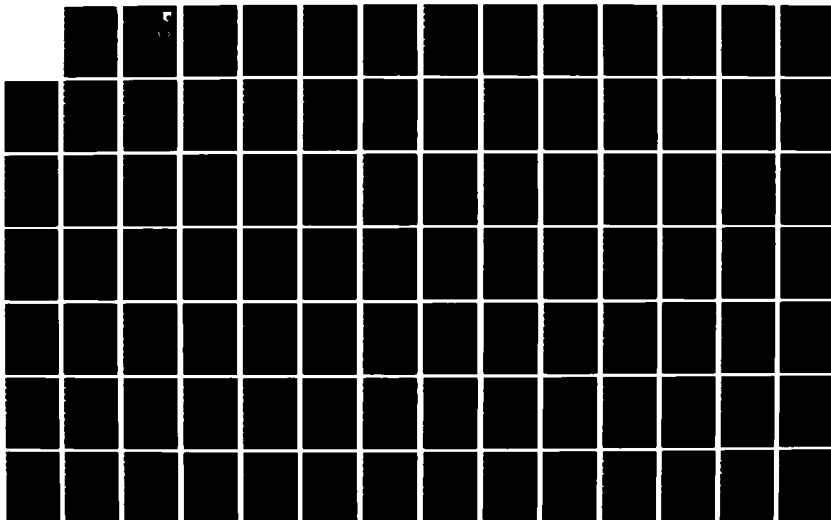
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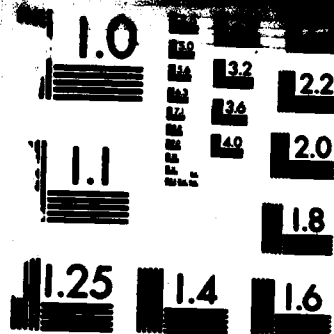
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CALCIUM/THIONYL CHLORIDE BATTERY TECHNOLOGY

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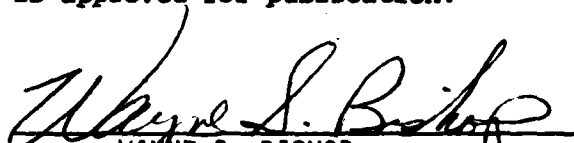
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This technical report has been reviewed and is approved for publication.


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<p>This final report documents the development efforts conducted by the Lithium Batteries Group of the Couples Department of Eagle-Picher Industries, in compliance with Air Force Contract F33615-81-C-2076. Technical effort was initiated in February 1982 and completed in June 1985.</p> <p>The objective of the project was to develop calcium-thionyl chloride cell technology. The original project was divided into two main tasks. Task One was to consist of component optimization and stability studies. Once sufficiently advanced, the ongoing results of Task One were to be integrated with Task Two. Task Two was to consist of demonstration of an optimized primary cell.</p> <p>In July, 1983, the program was redirected. Task Two was split, with effort to be directed toward both the original primary cell and toward a high discharge rate reserve configuration cell. Additional electrolyte salts were to be evaluated as a means of improving the storability of the active calcium-thionyl chloride cell.</p>					
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The primary (wet) cell was to be a hermetically sealed stainless steel cell of 3.2 in³ volume. The performance goal for the cell was 14 AH discharge life above 2.0V under a constant 400 ma discharge rate. Desired energy density was to be above 200 watt-hours/lb. Desired storage life was to be five years minimum.

The reserve cell desired was to be a 3.2 in³ cell also. A battery constructed of these cells was desired to supply 305 watt-hours continuous for twenty-one minutes at 28 ± 2 volts.

Active Cell Conclusions

Two major unresolved problem areas emerged from the work accomplished on the calcium-thionyl chloride system. By far the most serious problem was the inability to develop an electrolyte salt, both stable relative to calcium and still capable of supporting a 400 ma draw rate with reasonable discharge life. Both LiAlCl_4 and $\text{Ca}(\text{AlCl}_4)$ based electrolytes were corrosive towards the calcium anode within at most a few weeks' time. Moisture level in the electrolyte, at least down to approximately 100 mg/l, did not materially affect corrosion rate or onset.

Dissolution of LiAlCl_4 in benzoyl chloride, followed by dilution with thionyl chloride at varying percentages, did produce an electrolyte stable towards calcium, at least for the duration time of the storability study (five months' time). The gain in storability of the cell system by use of benzoyl chloride must be balanced against a steep loss in discharge life and current draw capability.

A wide variety of alternative electrolyte salts/inhibitors/additives were investigated. Of those that showed preliminary compatibility/storability with calcium, none investigated showed sufficient solubility to produce an electrolyte, or where they were sufficiently soluble, failed to produce open circuit voltages above 2.0 volts.

The second area unresolved in the development of the desired cell is a cathode sufficiently tolerant of discharge product plugging. Cathode discharge life for the desired 14 AH cell requires the cathode utilization rate to approach 1.2 AH/cm³. As developed, cathodes for the active cell produced 0.5-0.7 AH/cm³, leaving the as-designed cells decidedly cathode limited.

Reserve Cell Conclusions

From the discharge results obtained, it does not appear possible to produce a cell using $\text{AlCl}_3/\text{LiCl}$ electrolyte that will sustain a 31 amp discharge above 2.0 volts. At a 22 amp discharge rate, cells stayed above 2.0 volts for only three minutes or less. As well, the heat produced by the high rate discharges increases the corrosive attack by the electrolyte on the calcium anode to the point that cell pressures in excess of 700 psi have been observed in as little as five minutes. The extremely quick pressure rise observed at rates as low as seven amps makes it unlikely that a practical reserve cell can be produced, at least with acidic electrolyte.

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SECTION I
INTRODUCTION

1.1 Background

This final report documents the development efforts conducted by the Lithium Batteries Group of the Couples Department of Eagle-Picher Industries, in compliance with Air Force Contract F33615-81-C-2076. Technical effort was initiated in February 1982 and completed in June 1985.

The objective of the project was to develop calcium-thionyl chloride cell technology. The original project was divided into two main tasks. Task One was to consist of component optimization and stability studies. Once sufficiently advanced, the ongoing results of Task One were to be integrated with Task Two. Task Two was to consist of demonstration of an optimized primary cell.

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The reserve cell desired was to be a 3.2 in³ cell also. A battery constructed of these cells was desired to supply 305 watt-hours continuous for 21 minutes at 28 ± volts.

SECTION II

INITIAL COMPONENT INVESTIGATIONS

2.1 Anode Development

Anode material containing 99% calcium, .72% magnesium, and .3% Aluminum, was obtained from Pfizer, Inc., Wallingford, CT. This material was rolled to .040 inch. The annealing process involved heating the calcium to 850°F under an argon atmosphere of .007 mm Hg. The purity on a metals basis was determined by atomic absorption. Storage of the calcium was under mineral oil. An improved purity of calcium was supplied by Alfa Products, Danvers, MA. This material was 99.8% calcium. The material was in the form of turnings' which were not annealed. Pfizer later produced another calcium foil containing 99.9% calcium on a metals basis. The major metal contaminant was magnesium at .027%. This foil was also annealed and stored under mineral oil.

Alfa Products supplied three calcium alloys. The Ca: Cu, Ca: Al, and Ca: Li contained 90% calcium. The materials were in ingot form and were not annealed. Another alloy, Ca: Hg, was produced in a glovebox at less than 10 ppm H₂O using Pfizer 99.97% calcium. The calcium amalgam was produced on the surface of the calcium by immersing the calcium in mercury. The calcium alloys' resistance to corrosion was evaluated through compatibility storage tests.

2.2 Electrolyte Materials

Thionyl chloride for use in the calcium storage tests was obtained from three sources: Lithcoa, Apache, and Eagle-Picher. Lithcoa supplied 1.5 M LiAlCl₄ electrolyte. Manufacturers' stated concentration was confirmed by Atomic Absorption detection of the metals present. Iron content was never more than 5 ppm. The color of the Lithcoa material was pale yellow. Apache supplied 1.4 M LiAlCl₄ electrolyte which was dark blue or black in color.

Hydrolysis products and HCl contaminants were determined using a Perkin-Elmer Acculab II I. R. Spectrophotometer. Quartz I. R. cells were dried before filling within a glove box containing less than 10 ppm H₂O. Spectrographs showing reduced transmission at the 3310 cm⁻¹ band indicates the presence of hydrolysis products. Reduced transmission at the 2770 cm⁻¹ and indicates the presence of HCl. From sample to sample, changes in contaminant concentrations were detected by the changes in the % of transmission.

Figure 1 is a spectrograph of Lithcoa 1.5 M LiAlCl₄ in thionyl chloride. Reduced transmission at 3310 cm⁻¹ indicates hydrolysis products contamination. Also indicated is the presence of HCl at 2770 cm⁻¹.

Figure 2 is a spectrograph of Apache 1.4 M LiAlCl₄ in thionyl chloride. Reduced transmission at 3310 cm⁻¹ indicates hydrolysis products contamination. HCl presence is confirmed at 2770 cm⁻¹. Comparing Figures 1 and 2 indicates that Lithcoa contains approximately the same amount of HCl contamination.

Other 1.5 M LiAlCl₄ electrolyte was produced by reacting AlCl₃ and LiCl in thionyl chloride at room temperature. Thionyl chloride was obtained from Eastman Kodak and Fluka. Figure 3 is a spectrograph of the Eastman Kodak material. The reduced transmission at 2770 cm⁻¹ indicates the presence of HCl. Figure 4 is a spectrograph of the Fluka material. Unknown contamination in the Fluka material resulted in reduced transmission at 3230 cm⁻¹. The HCl content in the Fluka material resulted in reduced transmission at 2770 cm⁻¹. The HCl content in the Fluka material appears to be greater than the HCl content in the Eastman Kodak material, Figure 3. The Eastman Kodak thionyl was chosen as the solvent in electrolyte preparation. Distillation, refluxing, and stripping failed to improve the purity of the Eastman Kodak material. The AlCl₃ and LiCl salts were supplied by Fluka.

SPECTRUM NO. 61
DATE 21 Feb 1982
SAMPLE LithCoa
5001 LithCoa 1.5 M
LiAlCl4 SOC12
SOURCE LithCoa
STRUCTURE _____

PATH 2.00 mm 2C
SOLVENT none
CONCENTRATION _____
PHASE liquid
COMMENTS seen in purity
cells against KBr
5001 (20)
ANALYST EH

INFRARED
SPECTROPHOTOMETER

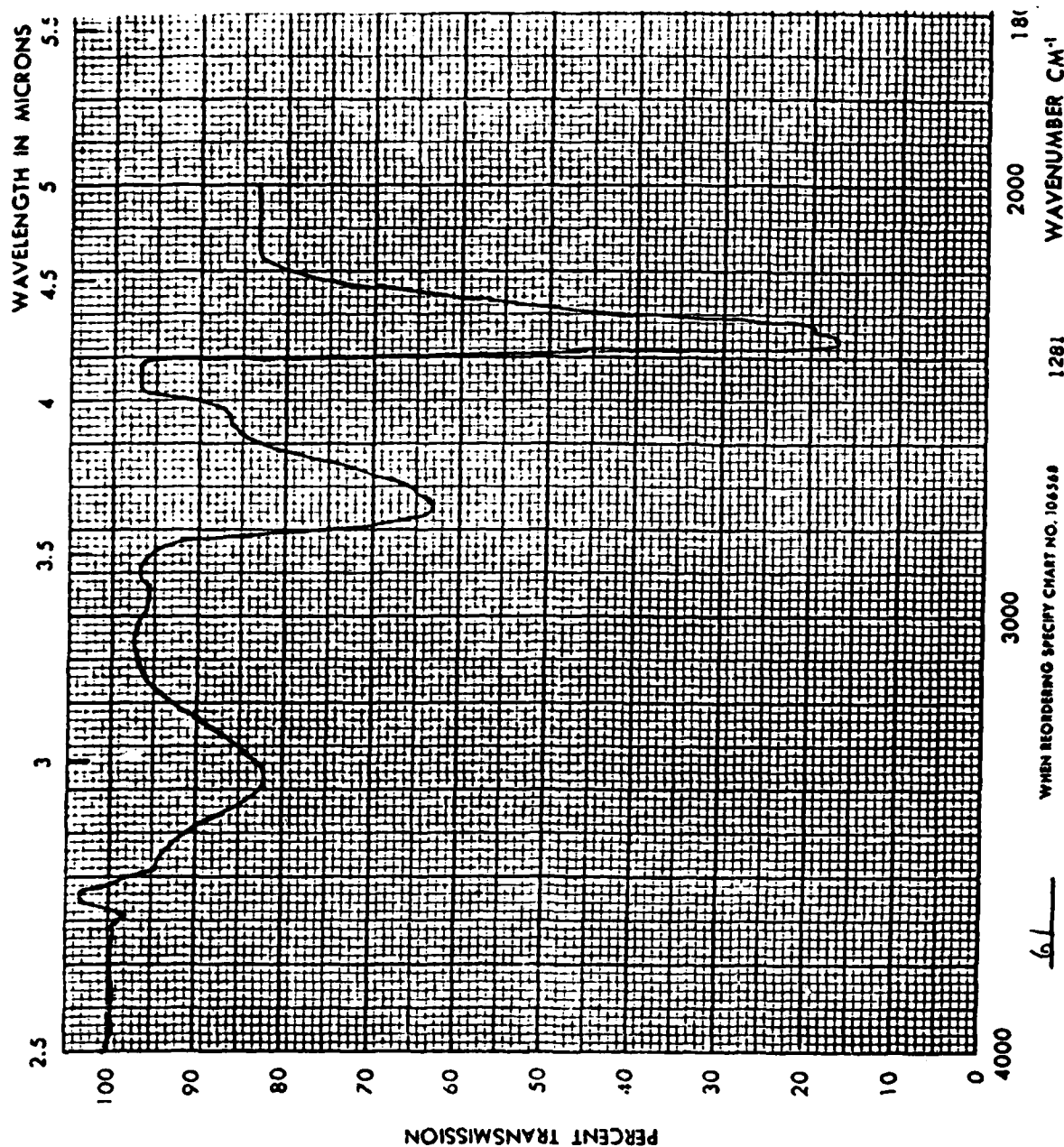


FIGURE 1 IR Scan - Lithcoa 1.5 M LiAlCl₄/SOCl₂

SPECTRUM NO. 60
 DATE 21 Oct 1982
 SAMPLE Apache SOCl₂
1.4 M LiAlCl₄
for 10179-1
 SOURCE Apache Chem Co.
 STRUCTURE _____

PATH 2.00 mm 2C
 SOLVENT neat
 CONCENTRATION _____
 PHASE liquid
 COMMENTS surrogate
cell against H₂O
SOCl₂ (2D)
 ANALYST FH

INFRARED
SPECTROPHOTOMETER

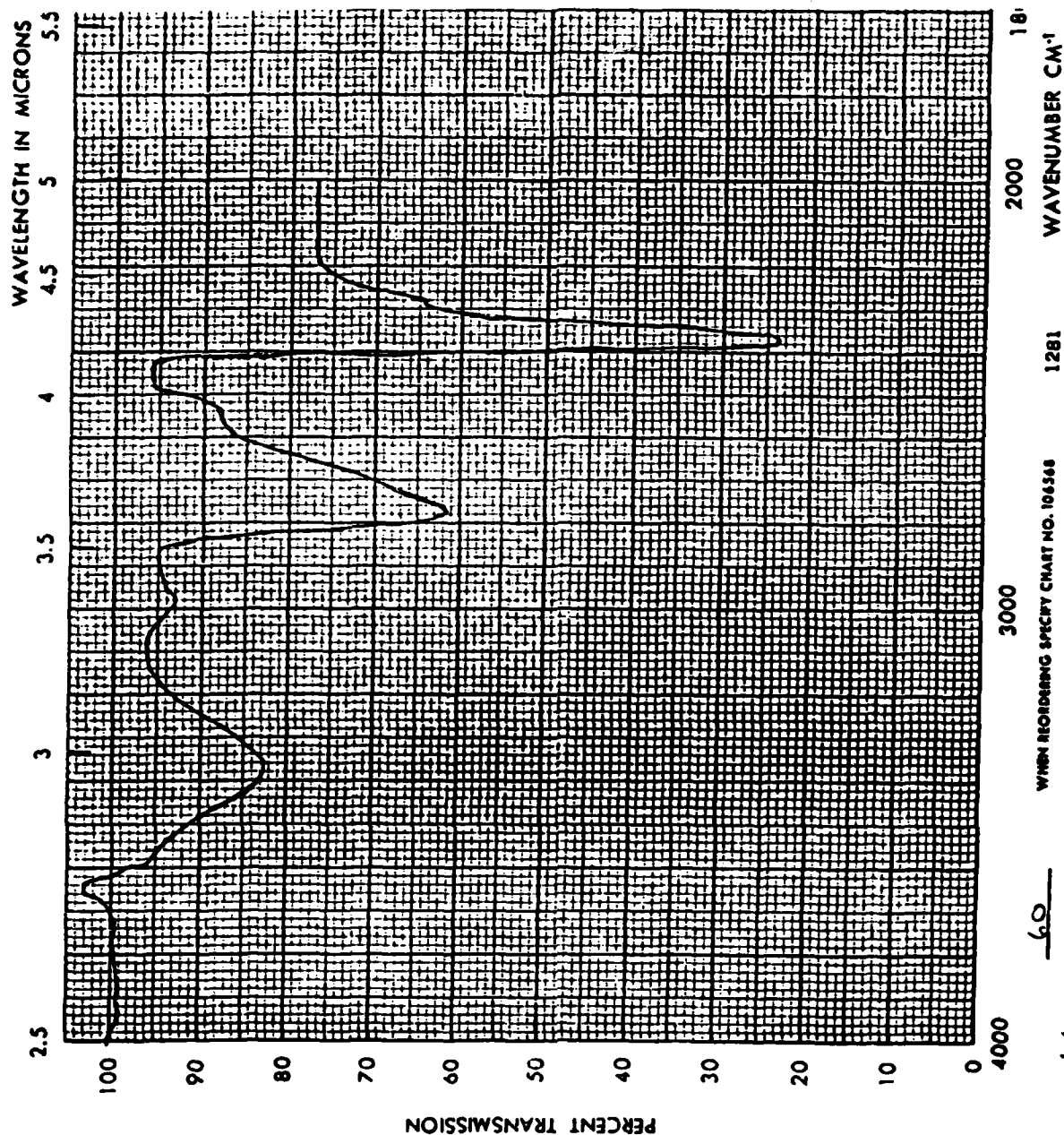
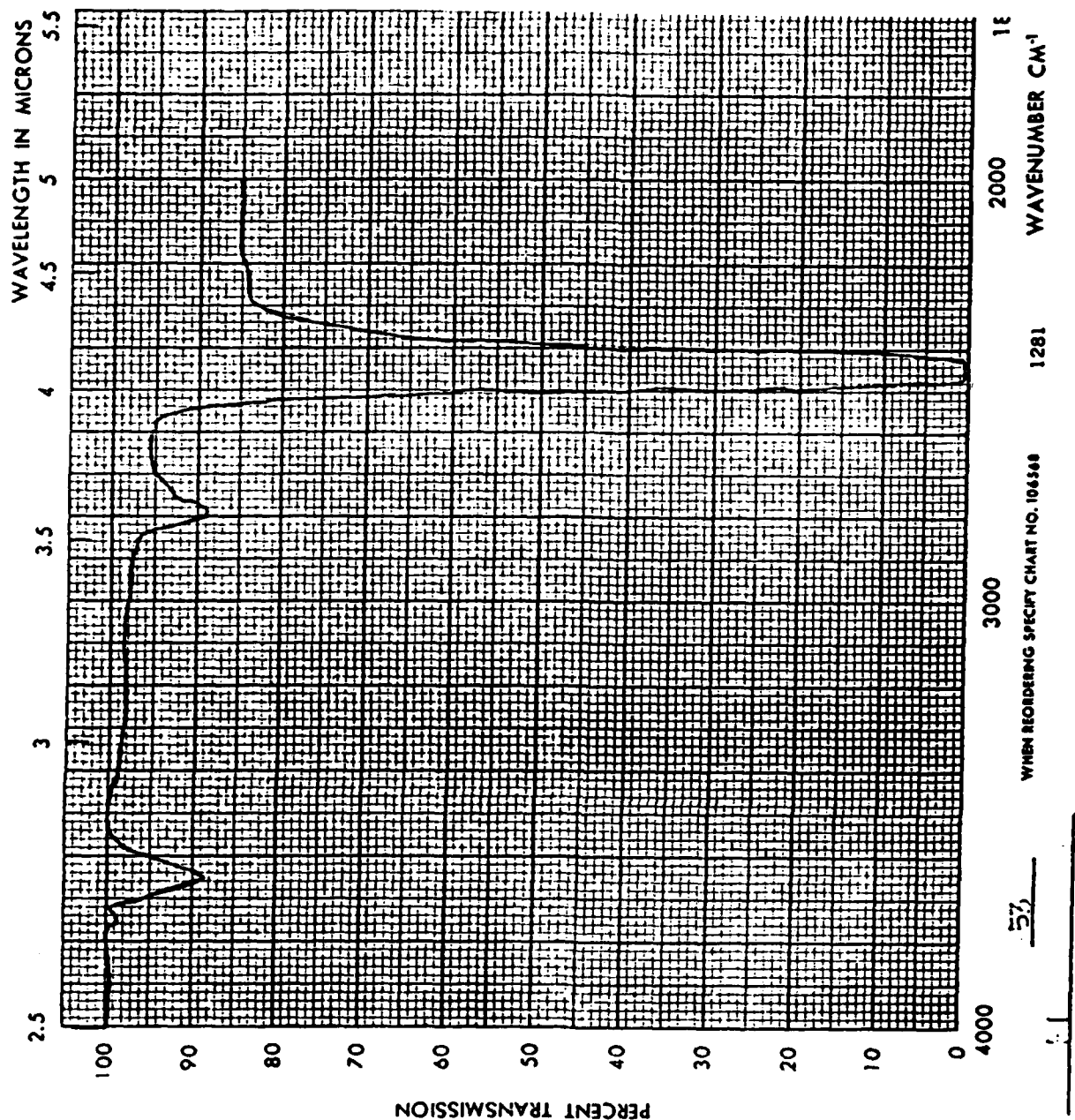


FIGURE 2 - IR Scan - Apache 1.4 M LiAlCl₄/SOCl₂



SPECTRUM NO. _____

DATE 07 Oct 1982

SAMPLE Kodak SOC12

As Received

SOURCE ED

STRUCTURE ORIGINAL

NATURAL

PATH 2.00 mm 2C; R=2D

SOLVENT acet

CONCENTRATION _____

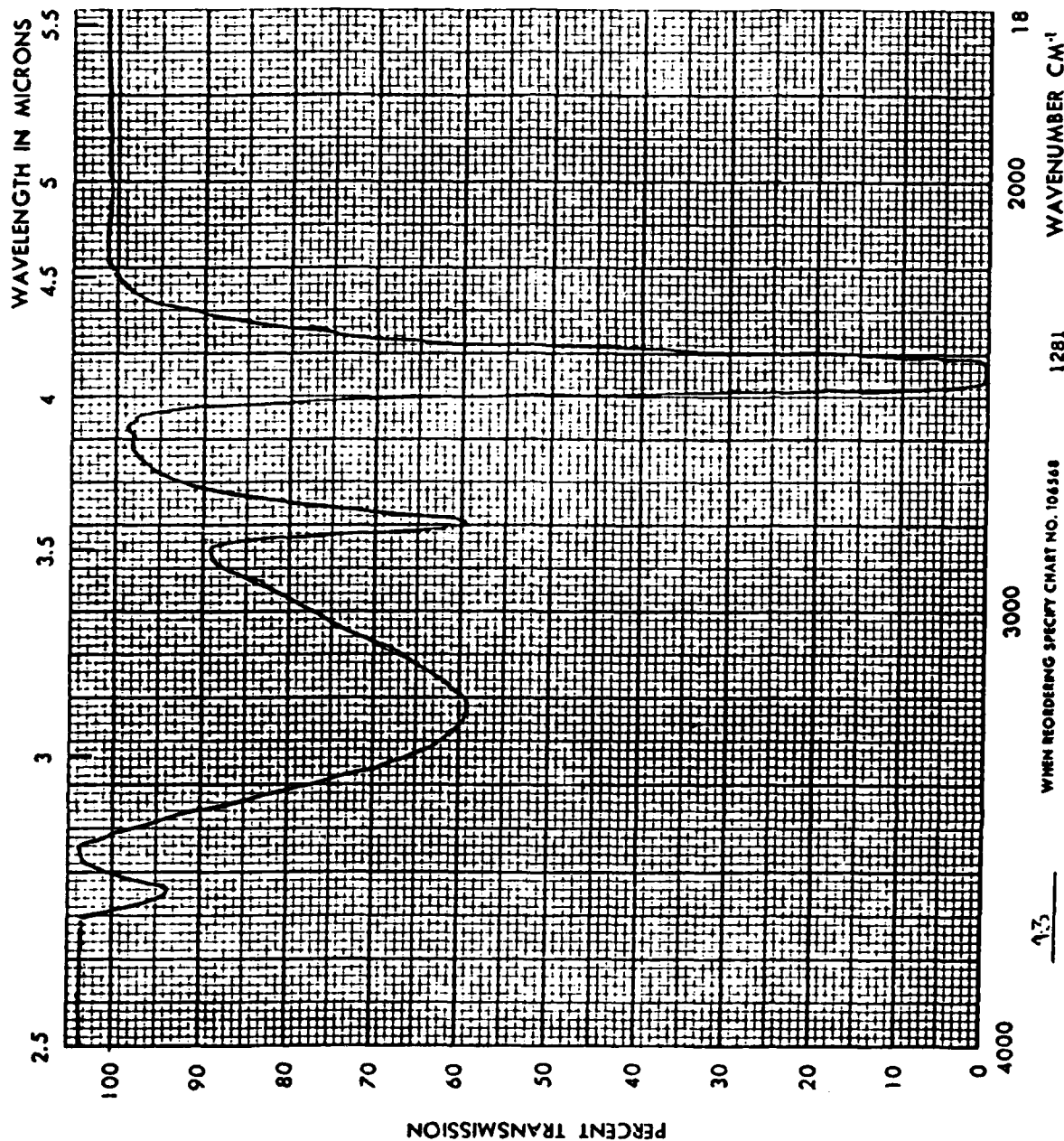
PHASE liquid

COMMENTS quality cells

ANALYST EFH

INFRARED
SPECTROPHOTOMETER

FIGURE 3 - IR Scan - Eastman Kodak SOC12



SPECTRUM NO. 43

DATE 26 Oct 1952

SAMPLE Fluka SOCl₂

Lot 31672 1051

SOURCE _____

STRUCTURE _____

PATH 2.00 mm 2A R: 2 B

SOLVENT neat

CONCENTRATION _____

PHASE liquid

COMMENTS Cell with 1

directly after run # 42

ANALYST EH

INFRARED
SPECTROPHOTOMETER

FIGURE 4 - IR Scan - Fluka SOCl₂

The first lot of 1.5 M LiAlCl_4 electrolyte was prepared in a glove box containing less than 10 ppm H_2O . All materials were used as received from the suppliers. Aluminum chloride was first dissolved in thionyl chloride. An excess amount of LiCl was then added to form LiAlCl_4 . The resulting electrolyte produced the spectrograph in Figure 5. Large amounts of hydrolysis products and HCl are indicated.

A second lot of 1.5 M LiAlCl_4 electrolyte was prepared using purified salts. The Fluka AlCl_3 was sublimed at +124C and 1 mm Hg. The Fluka LiCl was dried at +160C and 1 mm for 16 hours. The mixing technique was identical to that of the first lot. The resulting electrolyte produced the spectrograph in Figure 6. This spectrograph indicates the electrolyte contains lower contaminant concentrations than the electrolytes represented in Figures 3, 4, and 5.

2.3 Separator Materials

Four separator materials have been evaluated in this program. Manning Paper Co. supplied two non-woven glass separators', one with binder and one without binder. The third material, manufactured by the Zicar Company, Florida, NY was an Yttria oxide base, non-woven separator with a binder. Initial testing consisted of thionyl chloride compatability tests. C. H. Dexter, also supplied a non-woven glass separator without binder.

2.4 Storage Tests

Combinations of various cell components, additives, and contaminants were sealed in glass ampoules and stored at elevated temperatures. Glass ampoules resistant to thionyl chloride were cleaned and dried prior to filling and sealing. Following filling and sealing the ampoules were placed in hot storage and observed at regular intervals. The components in any ampoule were considered incompatible when either of the following changes were observed:

SPECTRUM NO. 59
 DATE Dec 17 52
 SAMPLE LiAlCl₄ EP

 SOURCE NaCl
 STRUCTURE _____

PATH 2.00 mm 20
 SOLVENT SOCl₂
 CONCENTRATION 1.5 F
 PHASE liquid soln
 COMMENTS run in quartz
cells against SOCl₂
(20)
 ANALYST EH

INFRARED
SPECTROPHOTOMETER

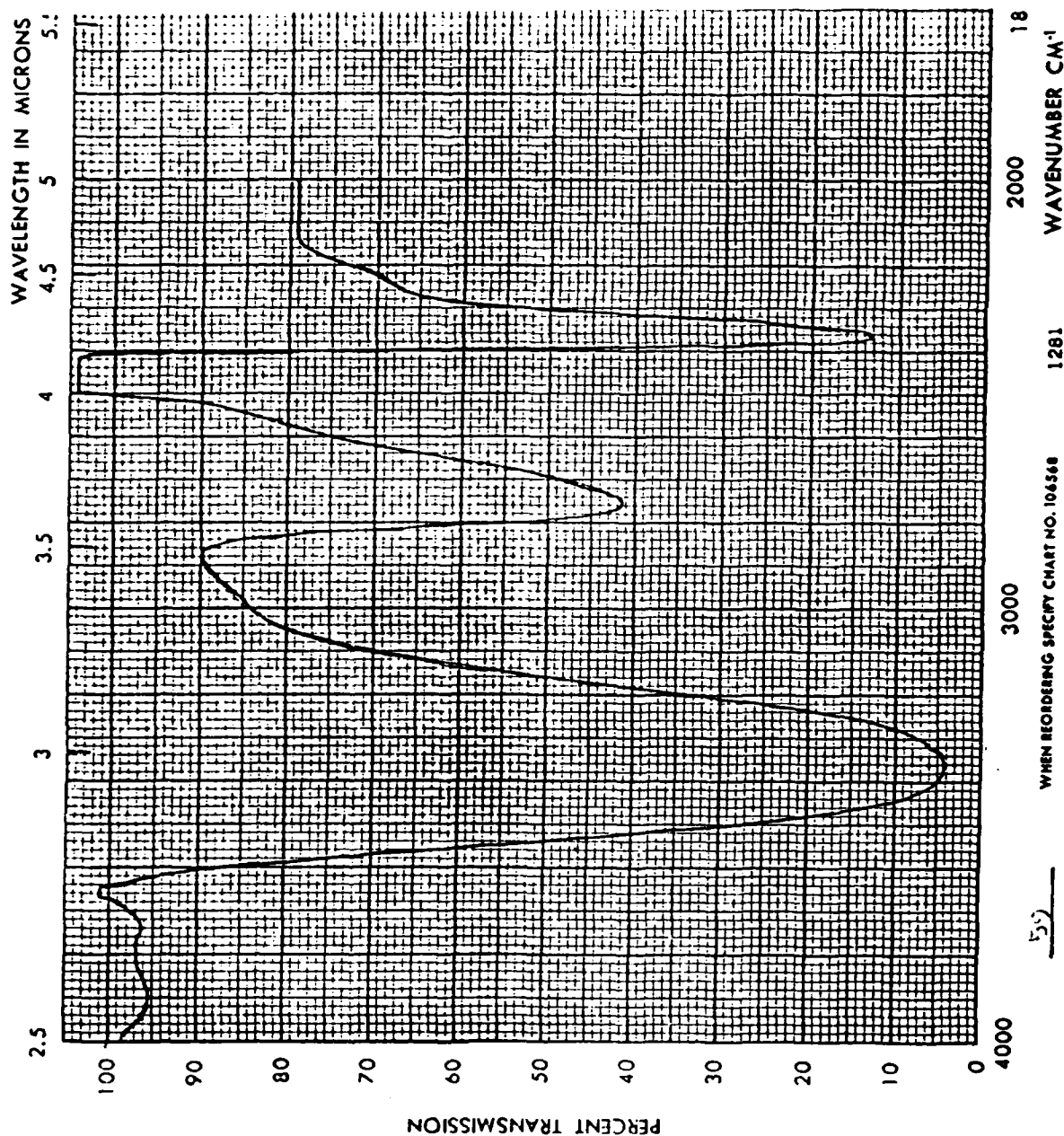


FIGURE 5 - IR Scan - E-P 1.5 M LiAlCl₄/SOCl₂

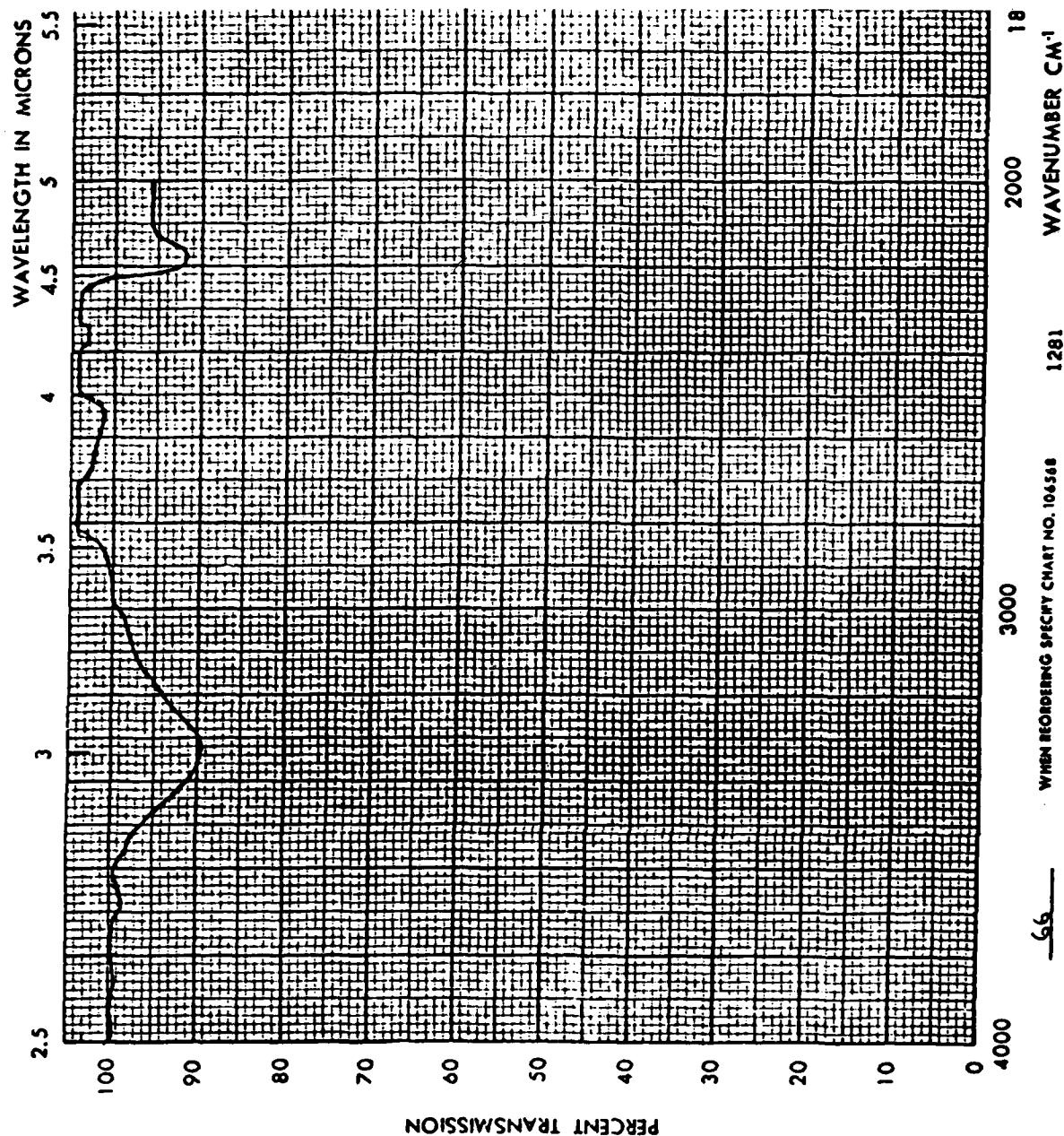


FIGURE 6 - IR Scan - E-P Electrolyte w/Sublimed AlCl₃

SPECTRUM NO. 66

DATE 25 Oct 1982

SAMPLE 19F-AlCl₃

Kaloh SOCl₂

SOURCE T. Potts

STRUCTURE _____

PATH 200 mm 2D

SOLVENT alcohol

CONCENTRATION _____

PHASE liquid

COMMENTS from inquiry

cell against Kaloh

SOCl₂ (2A)

ANALYST ETP

INFRARED
SPECTROPHOTOMETER

- 1) Electrolyte color or clarity.
- 2) Calcium pitting or corrosion.

Table 1 lists all materials and combinations used in the first ampoule test at +55 C. Table 1 shows 99% purity Pfizer calcium, 99.99% purity Alfa calcium, Manniglass separator with binder, and Yttria oxide separator have each reacted with thionyl chloride solvent or electrolyte. Lithium, magnesium and aluminum were tested for comparison. Ampoules containing calcium and thionyl chloride doped with 5% water (H_2O) and 5% sulfur have stored for 23 weeks with no indications of corrosion or chemical changes. Ampoules containing 1.5 M $LiAlCl_4$ electrolyte produced calcium corrosion after 6 weeks of storage. This same electrolyte caused the binder in the Manniglass separator to react with the electrolyte. Lithium, however, has stored 23 weeks in the electrolyte before the surface color had turned dark gray in color. The Yttria oxide separator was not affected.

Ampoules containing 0.5 M $Ca(AlCl_4)_2$ electrolyte resulted in calcium corrosion after 1 week of storage. Lithium corroded after 2 weeks of storage. This electrolyte also caused the Manniglass binder to dissolve. Yttria oxide has not been affected.

As a possible alternate solvent, sulfuryl chloride was evaluated in the storage test. Table 2 shows calcium, lithium, magnesium, aluminum, Manniglass with binder, and Yttria oxide separator to be unaffected by the sulfuryl chloride solvent. Addition of either $LiAlCl_4$ or $Ca(AlCl_4)_2$ resulted in ampoule failure in all cases except the Yttria oxide separator. In most cases failure was observed after 2 weeks of storage.

TABLE 1 - AMPOULE STORAGE TEST NO. 1

ALL AMPOULES STORED AT 130°F			E.T.
AMPULE COMPONENTS		PASS/FAIL	(WEEKS)
SOCl ₂ (Eastman)			
Ca (Pfizer)	Pass	23	
Ca (Alfa)	Pass	23	
Li	Pass	23	
Mg	Pass	23	
Al	Pass	23	
Manniglass (1400 with binder)	Pass	23	
Yttria Oxide	Pass	23	
SOCl ₂ + 5% Sulfur (Eastman)			
Ca (Pfizer)	Pass	23	
Ca (Alfa)	Pass	23	
Li	Pass	23	
Mg	Pass	23	
Al	Pass	23	
Manniglass (1400 with binder)	Pass	23	
Yttria Oxide	Pass	23	
SOCl ₂ + 5% H ₂ O (Eastman)			
Ca (Pfizer)	Pass	23	
Ca (Alfa)	Pass	23	
Li	Pass	23	
Mg	Pass	23	
Al	Pass	23	
Manniglass (1400 with binder)	Pass	23	
Yttria Oxide	Pass	23	
SOCl ₂ + 1.5M LiAlCl ₄ (Lithcoa)			
Ca (Pfizer)	Fail	6	
Ca (Alfa)	Fail	6	
Li	Fail	23	
Mg	Fail	2	
Al	Fail	2	
Manniglass (1400 with binder)	Fail	2	
Yttria Oxide	Pass	23	
SOCl ₂ + 0.5M Ca (AlCl ₄) ₂ (E-P)			
Ca (Pfizer)	Fail	1	
Ca (Alfa)	Fail	1	
Li	Fail	2	
Mg	Fail	2	
Al	Fail	2	
Manniglass (1400 with binder)	Fail	2	
Yttria Oxide	Pass	23	

TABLE 1 - (continued)

ALL AMPOULES STORED AT 130°F AMPULE COMPONENTS	PASS/FAIL	E.T. (WEEKS)
SO ₂ Cl ₂ (Eastman)		
Ca (Pfizer)	Pass	23
Ca (Alfa)	Pass	23
Li	Pass	23
Mg	Pass	23
Al	Pass	23
Manniglass (1400 with binder)	Pass	23
Yttria Oxide	Pass	23
SO ₂ Cl ₂ + 1.5M LiAlCl ₄ (E-P)		
Ca (Pfizer)	Fail	1
Ca (Alfa)	Fail	1
Li	Fail	2
Mg	Fail	2
Fl	Fail	2
Manniglass (1400 with binder)	Fail	2
Yttria Oxide	Pass	23
SO ₂ Cl ₂ + 0.5M Ca (AlCl ₄) ₂ (E-P)		
Ca (Pfizer)	Fail	1
Ca (Alfa)	Fail	1
Li	Fail	2
Mg	Fail	2
Al	Fail	2
Manniglass (1400 with binder)	Fail	2
Yttria Oxide	Pass	23
SO ₂ Cl ₂ (Fluka)		
Ca (Pfizer)	Pass	23
Ca (Alfa)	Pass	23
Ca (PF 99.97)	Pass	23
Li	Pass	23
Mg	Pass	23
Al	Pass	23
Ca:Li (90.10 Alfa)	Pass	23
Manniglass (1400 with binder)	Pass	23
Yttria Oxide	Pass	23
Ca (PF 99.97)		
SOCl ₂	Pass	21
SOCl ₂ + 5% Sulfur	Pass	21
SOCl ₂ + 5% H ₂ O	Pass	21
SOCl ₂ + 1.5M LiAlCl ₄ (Lithcoa)	Fail	6
SOCl ₂ + 0.5M Ca(AlCl ₄) ₂	Fail	1
SO ₂ Cl ₂ (Eastman)	Pass	21
SO ₂ Cl ₂ + 1.5M LiAlCl ₄	Fail	1
SO ₂ Cl ₂ + 0.5M Ca (AlCl ₄) ₂	Fail	1

TABLE 1 - (continued)

ALL AMPOULES STORED AT 130°F			E.T.
AMPULE COMPONENTS		PASS/FAIL	(WEEKS)
Ca:Li (90:10 Alfa)			
SOC1 ₂ (Eastman)		Pass	21
SOC1 ₂ + 5% S		Pass	21
SOC1 ₂ + 5% H ₂ O		Pass	21
SOC1 ₂ + 1.5M LiAlCl ₄ (Lithcoa)		Fail	1
SOC1 ₂ + 0.5M Ca (AlCl ₄) ₂		Fail	1
SO ₂ Cl ₂		Pass	21
SO ₂ Cl ₂ + 1.5M LiAlCl ₄		Fail	1
SO ₂ Cl ₂ + 0.5M Ca(AlCl ₄) ₂		Fail	1
Dexter (without binder)			
SOC1 ₂ + 1.5M LiAlCl ₄ (Lithcoa)		Pass	21
SOC1 ₂ + 0.5M Ca(AlCl ₄) ₂		Pass	21
SO ₂ Cl ₂ + 1.5M LiAlCl ₄		Pass	21
SO ₂ Cl ₂ + 0.5M Ca(AlCl ₄) ₂		Pass	21
SOC1 ₂ + 1.5M LiAlCl ₄			
Ca		Fail	6
Ca (w/Cyanoacrylate Film)		Fail	6
Manniglass (without binder)		Pass	19
SOC1 ₂ + 0.5M Ca(AlCl ₄) ₂			
Ca		Fail	1
Ca (w/Cyanoacrylate Film)		Fail	1
Manniglass (without binder)		Pass	19
SOC1 ₂ + 1.5M LiAlCl ₄	Ca:1 (90:10)	Fail	2
SOC1 ₂ + 1.0M Ca(AlCl ₄) ₂	Ca:Al(90:10)	Fail	2
SO ₂ Cl ₂ + 1.5M LiAlCl ₄	Ca:Cu(90:10)	Fail	2
SO ₂ Cl ₂ + 0.5M (Ca(AlCl ₄) ₂)	Ca:Cu(90:10)	Fail	2
SOC1 ₂ + 1.5M LiAlCl ₄	Ca (PF 99.97)	Fail	6
SOC1 ₂ + 1.0M LiAlCl ₄	Ca (PF 99.97)	Fail	6
SOC1 ₂ + 0.5M LiAlCl ₄	Ca (PF 99.97)	Fail	6
SOC1 ₂ + 1.5M LiAlCl ₄ + Ca (PF 99.97 +			
Cobalt Phthalocyanine		Fail	5
Iron Phthalocyanine		Fail	5
Lithium Perchlorate		Fail	1
Rhodium on Carbon Black		Fail	1
Tetraethyl Ammonium Perchlorate		Fail	1
Mg Perchlorate		Fail	1

TABLE 2 - AMPOULE STORAGE TEST NO. 2

START AT 130 F	AMPULE COMPONENTS	PASS/FAIL	(WEEKS)	ID
Ca + 1.5M	LiAlCl ₄ + SOCl ₂ (Ca polished)	Fail	6	3
Ca + 1.5M	LiAlCl ₄ + SOCl ₂ 1 min. to air	Fail	4	7
Ca + 1.5M	LiAlCl ₄ + SOCl ₂ 4 min. to air	Fail	4	11
Ca + 1.5M	LiAlCl ₄ + SOCl ₂ 8 min. to air	Fail	4	15
Ca + 1.0M	Li ₂ B ₁₀ Cl ₁₀ + SOCl ₂ (Ca unpolished)	Fail	7	19
Ca + 0.17M	Li ₂ B ₁₀ Cl ₁₀ + SOCl ₂ +(Ca unpolished)	Fail	7	20
Ca + 0.17M	Li ₂ B ₁₀ Cl ₁₀ + SOCl ₂ +(Ca polished)	Fail	7	21
Ca + 1.5M	LiAlCl ₄ + SOCl ₂ (Ca polished)	Fail	7	22
Ca + 1.5M	LiAlCl ₄ + SOCl ₂ (Ca unpolished)	Fail	7	26
Ca + 1.2M	LiGaCl ₄ + SOCl ₂ (Ca unpolished)	Fail	7	30
Ca + 1.5M	LiAlCl ₄ + SOCl ₂ (Ca polished)	Fail	7	34
Ca + 1.5M	LiAlCl ₄ + SOCl ₂ (Ca unpolished) excess LiCl	Fail	7	38

Ca Annealed Ca supplied by Pfizer

AlCl₃ Sublimed by E.P.I.

LiCl Dried at 160°C 7 x 10⁻³ mm Hg for 16 hours

GaCl₃ As received from Aldrich Chemical Company

SOCl₂ As received from Eastman Kodak

Li₂B₁₀Cl₁₀ Dried at 160°C 7 x 10⁻³ mm Hg for 16 hours

Table 1 shows that an alloy containing 90% calcium and 10% lithium was corrosion resistant in sulfuryl chloride and thionyl chloride. Corrosion was observed after 1 week when the alloy was stored with LiAlCl_4 or $\text{Ca}(\text{AlCl}_4)_2$ electrolytes. The Dexter glass separator without binder was inert to LiAlCl_4 and $\text{Ca}(\text{AlCl}_4)_2$ electrolytes.

Ampoules in Table 1 show that cyanoacrylate film did not lengthen the storage time of calcium in 1.5 M LiAlCl_4 . The cyanoacrylate film was formed by successively dipping polished calcium foil into a solution of methylethylketone and cyanoacrylate ester until a .003 inch thick film had formed on each side of the calcium foil. The calcium and 1.5 M LiAlCl_4 electrolyte was sealed within an ampoule.

Two calcium alloys, one containing 10% aluminum and the other containing 10% copper, both failed at resisting corrosion in either 1.5 M LiAlCl_4 electrolyte or 0.5 M $\text{Ca}(\text{AlCl}_4)_2$ electrolyte. Electrolytes using either thionyl chloride or sulfuryl chloride were used. In all cases, storage lasted no longer than 2 weeks before corrosion was observed.

Ampoules in Table 1 show Pfizer calcium of 99.97% purity to store no more than 6 weeks in 1.5 M LiAlCl_4 electrolyte. Pfizer calcium having 99% purity, also stored for no more than 6 weeks in 1.5 M LiAlCl_4 .

The materials cobalt phthalocyanine, iron phthalocyanine, lithium perchlorate, rhodium-on-carbon black, tetraethylammonium perchlorate, and magnesium perchlorate were believed to be conductivity enhancers, passive layer formers, or catalysts. Their compatibility in 1.5 M LiAlCl_4 electrolyte along with 99.97% purity Pfizer calcium is shown in Table 1. There was no additive which could improve or equal the storage time of 6 weeks.

Table 2 summarizes a second storage test of 130°F (+55°C). Ampoules 7, 11 and 15 were exposed to 5% R. H. air for 1, 4, and 8 minutes respectively (in order to increase the hydrolysis contamination). Figures 7, 8, and 9 show spectrographs of the hydrolysis contamination. In all cases calcium corrosion was observed after no more than 4 weeks of storage. Typical storage time for calcium in 1.5 M LiAlCl_4 with minimum hydrolysis contamination has been 6 weeks.

Table 2 ampoule Nos. 19, 20, and 21 show the use of $\text{Li}_2\text{B}_{10}\text{Cl}_{10}$ as an alternate electrolyte salt failed to increase the storage time over 1.5 M LiAlCl_4 , likewise the use of 1.2 M LiGaCl_4 , Table 2, failed to improve the storage time.

Since the presence of unreacted AlCl_3 in the electrolyte may be the cause of the corrosion, an ampoule containing excess LiCl was constructed in order to determine if excess LiCl would inhibit the corrosion. Ampoule No. 38 in Table 2 shows that calcium corrosion was again observed after 7 weeks of storage. Calcium corrosion in 1.5 M LiAlCl_4 appears to be independent of surface preparation since polished and unpolished calcium both stored for approximately 7 weeks, as shown by ampoule Nos. 22 and 26 in Table 2.

The materials and combinations of the third ampoule test are listed in Table 3. This storage test was at +75°C. The results show that calcium in 1.5 M LiAlCl_4 electrolyte showed corrosion at 4 weeks. The use of SO_2 and vinyl polymer additives did not retard the corrosion. Calcium and 0.15 M LiAlCl_4 electrolyte also showed corrosion at 4 weeks, indicating that a reduced LiAlCl_4 concentration did not increase the storage time. Calcium with 1.5 M LiGaCl_4 and 1.14 M $\text{Ca}(\text{GaCl}_4)$ both showed corrosion at 4 weeks.

TABLE 3 AMPOULE STORAGE TEST NO. 3

ALL AMPOULES STORED AT +75°C AMPULE COMPONENTS	PASS/FAIL	E.T. (WEEKS)	ID
Ca + SOCl ₂	Pass	4	54
Ca + SOCl ₂ + 2.1% SO ₂	Pass	4	58
Ca + SOCl ₂ + 8.3% SO ₂	Pass	4	62
Ca + SOCl ₂ + 0.1% Vinyl Polymer	Pass	4	66
Ca + SOCl ₂ + 0.5% Vinyl Polymer	Pass	4	70
Ca + SOCl ₂ + 1.5M LiAlCl ₄	Fail	4	74
Ca + SOCl ₂ + 2.1% SO ₂ + 1.5M LiAlCl ₄	Fail	4	78
Ca + SOCl ₂ + 8.3% SO ₂ + 1.5M LiAlCl ₄	Fail	4	82
Ca + SOCl ₂ + 0.1% Vinyl Polymer + 1.5M LiAlCl ₄	Fail	4	86
Ca + SOCl ₂ + 0.5% Vinyl Polymer + 1.5M LiAlCl ₄	Fail	4	90
Ca + SOCl ₂ + 0.15M LiAlCl ₄	Fail	4	94
Ca + SOCl ₂ + 1.5M LiGaCl ₄	Fail	4	98
Ca + SOCl ₂ + 1.14M Ca (GaCl ₄) ₂	Fail	4	102
Ca + SOCl ₂ + 1.5M (CH ₃) ₄ NCl	Pass	4	106
Ca + SOCl ₂ + SOCl ₂ + C ₆ H ₅ CH ₂ N(CH ₃) ₃ Cl	Fail	4	110
Ca + SOCl ₂ + Hg + 1.5M LiAlCl ₄	Fail	4	114
Ca	99.97% Pfizer		
LiAlCl ₄ 1.5M in SOCl ₂	Lithcoa		
GaCl ₃	Aldrich Chemical		
SOCl ₂	Eastman Kodak		
SO ₂	Matheson		
Vinyl Polymer	Union Carbide		
(CH ₃) ₄ NCl	Aldrich		
C ₆ H ₅ CH ₂ N(CH ₃) ₃ Cl	Hexcel		

SPECTRUM NO. 70
 DATE 12-29-42
 SAMPLE Lithcoa 15M51A14
in SOCl₂ 487743
 SOURCED Lithcoa
 STRUCTURE _____
 PATH 1.00 mm 1A
 SOLVENT accl
 CONCENTRATION _____
 PHASE _____
 COMMENTS run against
LiAlH₄ SOCl₂
 ANALYST FA

INFRARED
SPECTROPHOTOMETER

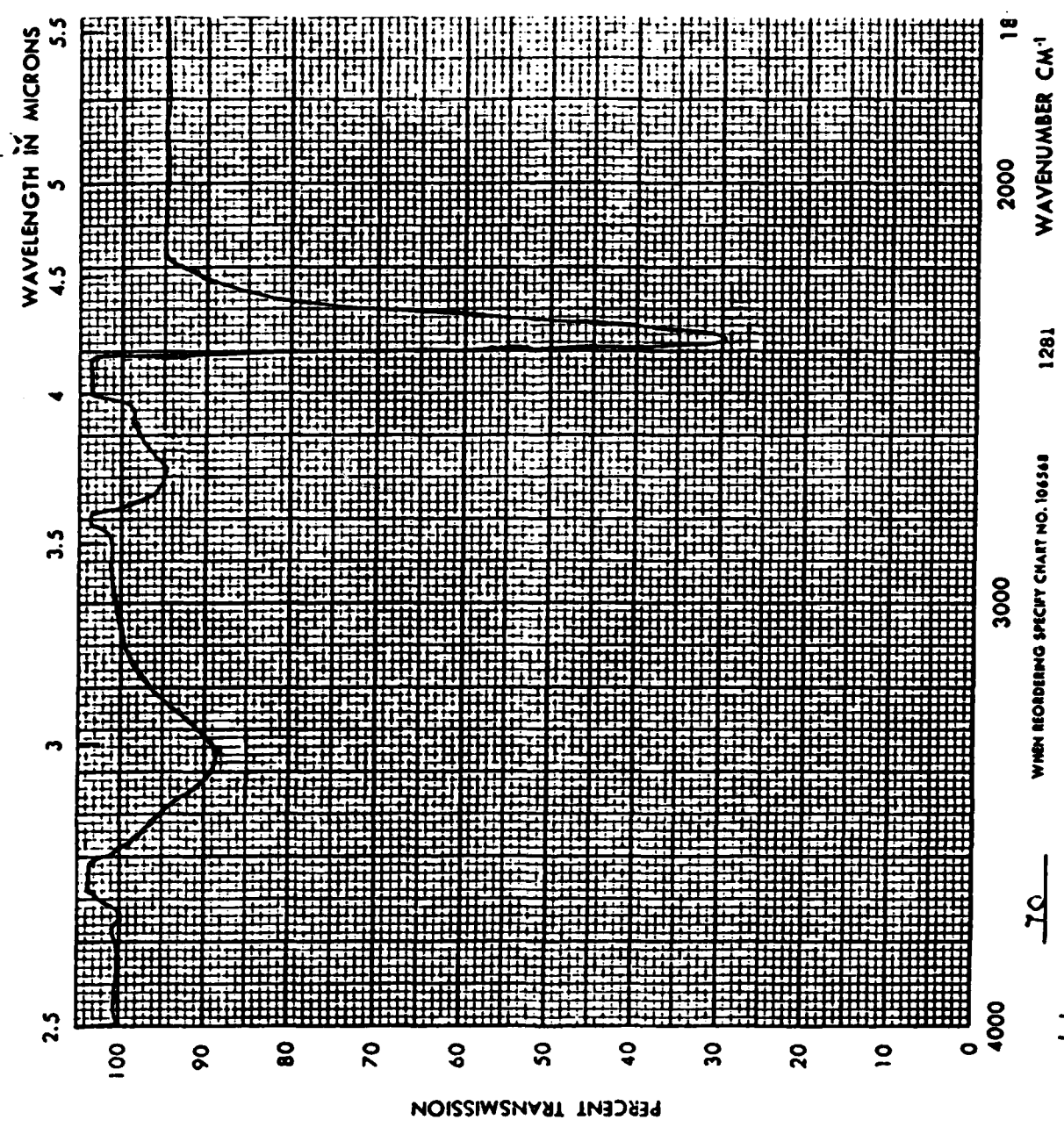


FIGURE 7 - IR Scan - Lithcoa Electrolyte Prior to Air Exposure

SPECTRUM NO. 72
 DATE 28 Oct 82
 SAMPLE 1.5 g LiAlCl₄
in SOCl₂
Exposed 4 min
 SOURCE Lithcoa
 STRUCTURE liquid

PATH 1.00 mm 1A
 SOLVENT meat
 CONCENTRATION
 PHASE
 COMMENTS seen against
Heated SOCl₂
 ANALYST EJH

INFRARED
SPECTROPHOTOMETER

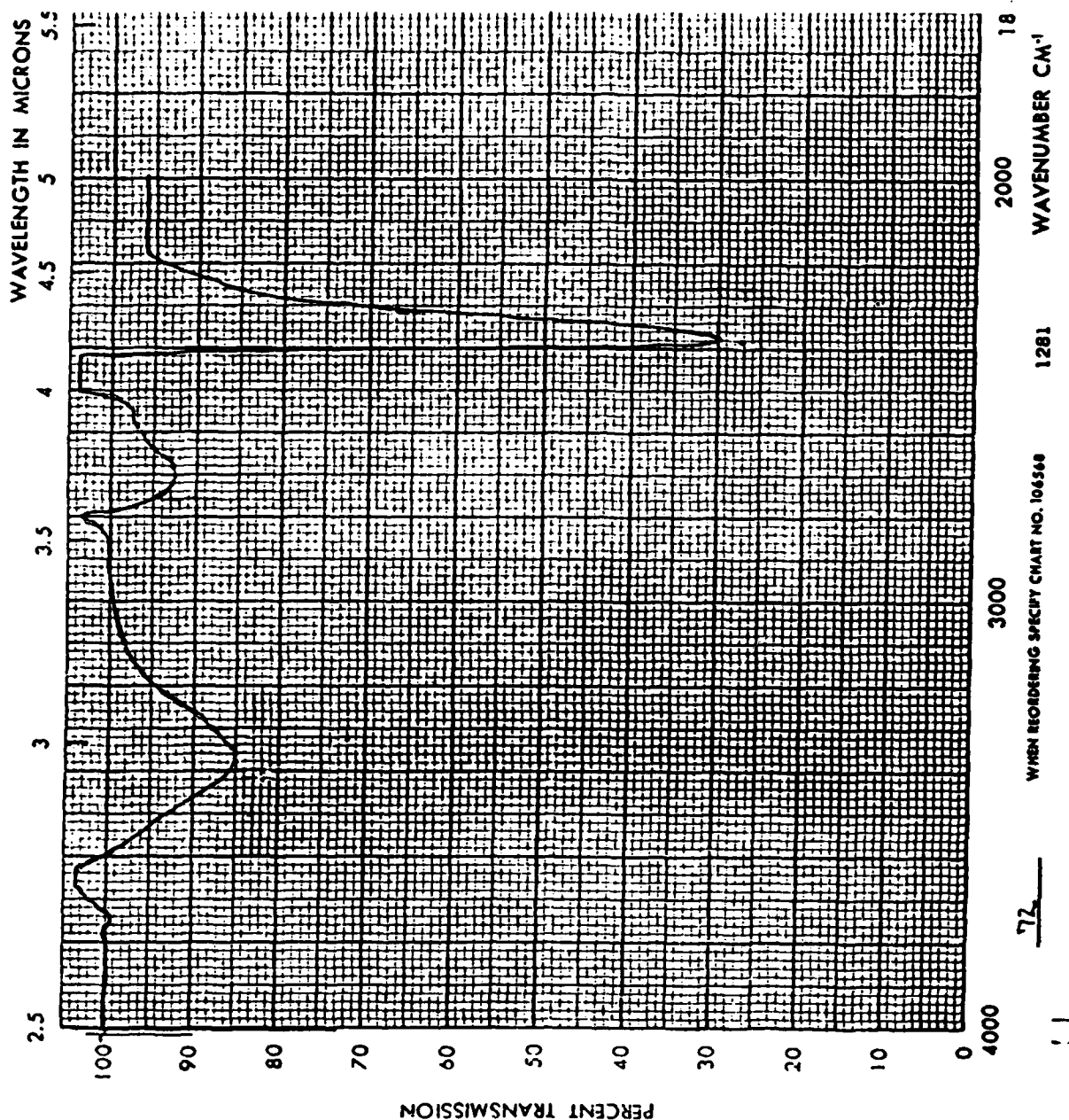


FIGURE 8 - IR Scan - Lithcoa Electrolyte w/4 Minute Air Exposure

SPECTRUM NO. 73
 DATE 28 Oct 82
 SAMPLE 1.54 FIAIC 14
in SOCl₂ exposed
Paris Drama
 SOURCE Kirk-Cad
 STRUCTURE Liquid

PATH 1.00 mm 11
 SOLVENT meat
 CONCENTRATION
 PHASE
 COMMENTS run against
Kodak SOCl₂
 ANALYST EH

INFRARED
 SPECTROPHOTOMETER

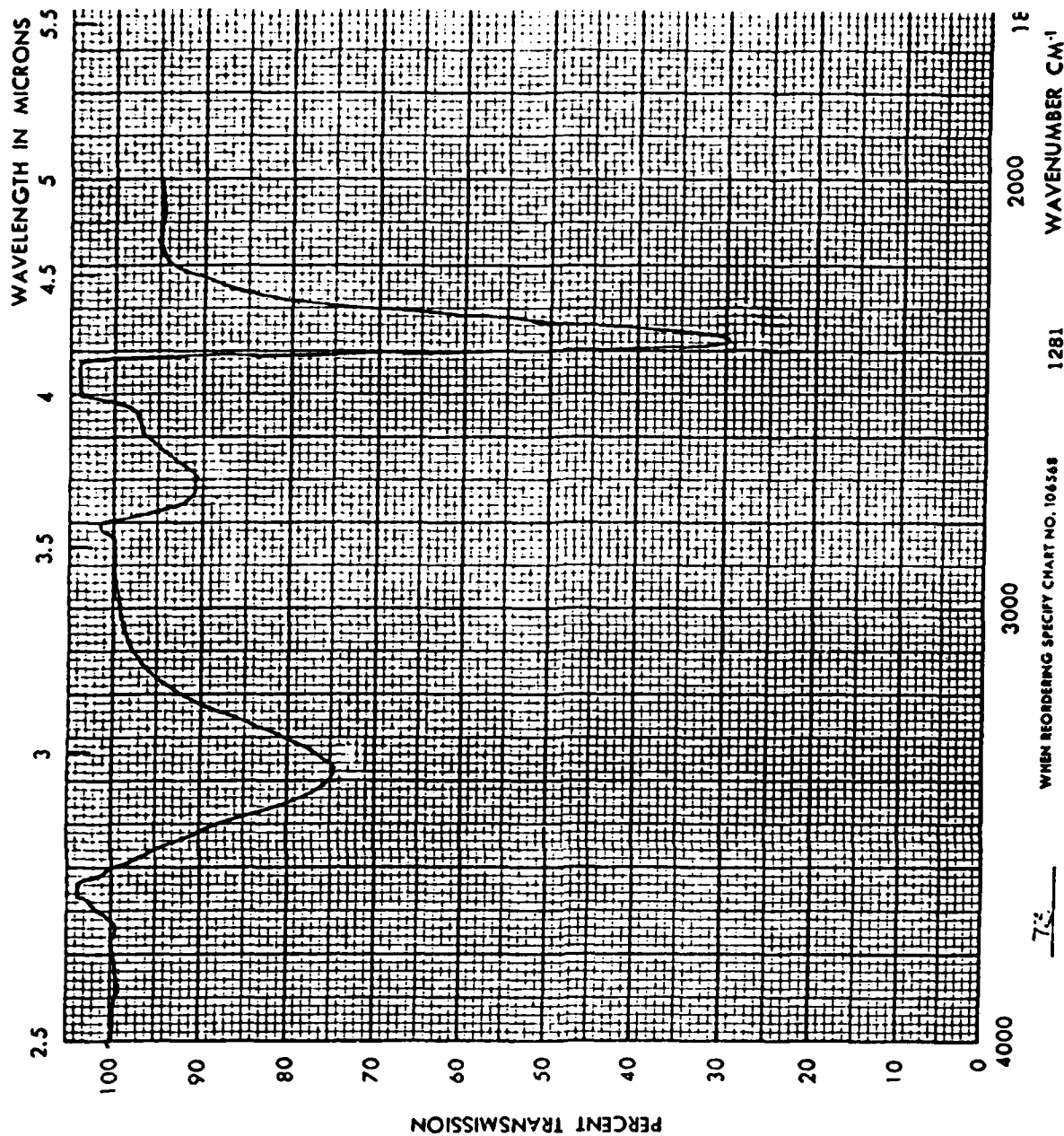


FIGURE 9 - IR Scan - Lithcoa Electrolyte 3/8 Minute Air Exposure

The ampoules containing the SO_2 and the vinyl polymer in thionyl chloride solvent produced no calcium corrosion after 4 weeks. Tetramethyl ammonium chloride electrolyte has produced no calcium corrosion and no discoloring in the ampoule. All components have remained in their original condition.

Electrolyte storage tests each containing a different separator material have shown that separator with binder is not compatible with the electrolyte. Table 1 showed Yttria oxide separator to be compatible with oxyhalides and oxyhalide electrolytes for 23 weeks at $+55^\circ\text{C}$. However, this separator has very poor mechanical and handling properties due to its loosely bound fibers.

Two types of Manniglass separator were evaluated through storage tests listed in Tables 1 and 2. Manniglass 1400 which contains a binder was found to be stable with oxyhalide solvents containing no salts. The presence of electrolyte salts in the solvent, however, produces a reaction with the binder. The Manniglass 1200 separator without the binder was found to be stable in thionyl chloride electrolytes containing either LiAlCl_4 or $\text{Ca}(\text{AlCl}_4)_2$ for 23 weeks at $+55^\circ\text{C}$. Both Manniglass separators have fair handling and mechanical properties.

Compatibility tests were set up using Dexter 255 glass separator containing no binder and have stored with various thionyl chloride electrolytes for 21 weeks at $+55^\circ\text{C}$. The Dexter material also has good handling and mechanical properties.

2.5 Electrolyte Development

Further efforts to eliminate the calcium corrosion in the presence of aluminum chloride included the use of an alternate or additional electrolyte salt. Also considered was the use of an oxyhalide other than thionyl chloride or a co-solvent to use with an oxyhalide which might improve the solubility of a non-corrosive salt. Oxyhalides considered were sulfuryl chloride (SO_2Cl_2), sulfur monochloride (S_2Cl_2), and sulfur dichloride (SCl_2). Co-solvents considered were acetone, dimethylsulfite, methylacetate, ethyl ether, carbon disulfide, benzene, carbon tetrachloride, and chloroform. Table 4 shows the co-solvent/oxyhalide compatibility matrix. Most materials were miscible in all proportions. Acetone was found to decompose in all oxyhalides. Dimethylsulfite decomposed in sulfuryl chloride and was compatible with the other oxyhalides.

Table 5 summarizes the salt/solvent compatibility test. Two salts appeared to be likely replacements for the aluminum containing salts in the electrolyte. Lithium decachlorodecaborate ($\text{Li}_2\text{B}_{10}\text{Cl}_{10}$) and benzyltrimethylammonium chloride ($\text{C}_{10}\text{H}_{16}\text{NCl}$) were each soluble in oxyhalide solvents, particularly thionyl chloride. The benzyltrimethylammonium chloride ($\text{C}_{10}\text{H}_{16}\text{NCl}$) failed a hot storage test with calcium metal at $+75^\circ\text{C}$ as shown in Table 3. Lithium decachlorodecaborate also failed to improve calcium storage as shown in Table 2.

Materials considered to replace aluminum chloride, or to act as an inhibitor in the calcium corrosion mechanism are summarized in Table 6. Four Group III chlorides were mixed with thionyl chloride at room temperature. Of the group only gallium trichloride produced an electrolyte following the addition of lithium chloride to the solution. Table 2 shows that calcium

TABLE 4 - CO-SOLVENT/OXYHALIDE MATRIX

	SOCl_2	SO_2Cl_2	SCl_2	S_2Cl_2
Acetone	M-D	D	D	D
DMSI	M	D	M	M
MeAcetate	M	M	M	M
Ethyl Ether	M	M	M	M
CS_2	M	M	M	M
C_6H_6	M	M	M	M
CCl_4	M	M	M	M
CHCl_3	M	M	M	M

M = Mixes

D = Decomposes

TABLE 5 - SALT/SOLVENT COMPATIBILITY MATRIX

	CS ₂	C ₆ H ₆	CCl ₄	CHCl ₃	Ethyl Ether	SOCl ₂	SO ₂ Cl ₂	SCl ₂	S ₂ Cl ₂
Ca(BF ₄) ₂	I	I	I	I	I	I	I	I	I
CaBr ₂	I	I	I	I	I	I	D	I	I
LiSCN	I	I	I	I	MS	D	D	D	I
Li ₂ B ₁₀	I	I	I	I	SS	VS	VS	D	SS
LiAsF ₆	I	I	I	MS	VS	I	I	I	I
C ₁₀ H ₁₆ NC1	I	I	I	VS	I	VS	VS	VS	SS
LiBF ₄	I	I	I	I	SS	I	I	I	I
K ₂ Cr ₂ O ₇	I	I	I	I	I	SS	I	I	I
LiNO ₃	I	I	I	I	I	D	I	I	SS
LiBr	I	I	I	I	SS	I	SS	I	I
MgClO ₄	I	I	I	I	SS	D	I	I	I

VS = Very soluble
 MS = Moderately soluble
 SS = Slightly soluble
 I = Insoluble
 M = Mixes
 S = Separates
 D = Decomposes

TABLE 6 - ELECTROLYTE SALTS AND INHIBITORS

SALTS

BCl_3	SbCl_5
GaCl_3	PCl_5
InCl_3	WCl_5
TiCl_3	TaCl_5
CaS	NbCl_5
$(\text{CH}_3)_4\text{NCl}$	SiCl_4
SnCl_2	SnCl_4

INHIBITORS

Formamide	Calcium Oxalate
Tetramethylammonium chloride	Calcium Acetate
Disodium Ethylenediaminetetraacetate	Calcium Propionate
Sodium Diethyldithiocarbamate	Propylene Oxide
Mercuric Acetate	Mesityl Oxide
Potassium Acetate	Mesitylene
Dimethyl Formamide	Diphenylamine
Calcium Stearate	Anthraquinone
	Arsenic III Chloride

storage in 1.5 M LiGaCl_4 was not improved over using 1.5 M LiAlCl_4 . The Group IVB and Group VB chlorides listed in Table 6 were found to readily dissolve in thionyl chloride to form 1.0 molar solutions. However, after 4 weeks of storage at $+75^\circ\text{C}$, only the WCl_5 was found to be compatible with calcium.

Tetramethylammoniumchloride $(\text{CH}_3)_4\text{NCl}$ in thionyl chloride was found to be stable with calcium. Table 3 shows 1.5 M $(\text{CH}_3)_4\text{NCl}$ and calcium have stored for no less than 4 weeks at $+75^\circ\text{C}$ with no calcium corrosion or electrolyte changes observed. The conductivity of $(\text{CH}_3)_4\text{NCl}$ at $+20^\circ\text{C}$ is similar to LiAlCl_4 solution.

Table 6 also lists materials which may act as corrosion inhibitors in the calcium/aluminum chloride electrolyte. Of the materials listed, formamide, tetramethylammoniumchloride, mercuric acetate, disodium ethylenediaminetetraacetate, potassium acetate, and sodium diethyldithiocarbamate all react with LiAlCl_4 electrolyte to form a heavy precipitate, making the co-use of these materials unlikely.

2.6 Electrochemical Investigation

A subcontractor, Pinnacle Research Institute, Inc., of Cupertino, California was utilized to conduct an electrochemical investigation into the corrosion mechanism of Ca and Li metals in lithium and calcium tetrachloroaluminate electrolytes. In their work, it was found that the anodic dissolution of Ca in $\text{LiAlCl}_4/\text{SOCl}_2$ and $\text{Ca}(\text{AlCl}_4)_2/\text{SOCl}_2$ proceeded by different mechanisms for each electrolyte when galvanostatic polarization methodology was employed. The $\text{Ca}(\text{AlCl}_4)_2$ electrolyte dissolution mechanism was AlCl_4 dependent, while a pure charge transfer reaction was observed for the LiAlCl_4 based electrolyte. The final Pinnacle report on this work is included as Appendix A to this report.

SECTION III

INITIAL CATHODE/ELECTROLYTE DEVELOPMENT

3.1 Cathode Development

Cathode development progress was determined by discharge in hermetically sealed glass test cells. Each glass cell would hold one cathode measuring 0.54 x 0.687 inches, two anodes, separator, and up to 20 cm³ of electrolyte. Each cell was constructed cathode limited in order to observe the total life and capacity of the cathode, with no capacity reductions caused by a shortage of anode or electrolyte materials.

Initial cathode material contained Shawinigan carbon black blended with a Teflon binder. The cathode material was dry pressed to an expanded nickel grid using a fabrication pressure of 15 LB/in² on the cathode surface. Cathode thickness varied with the amount of cathode mix used. The pressed cathodes were then dried at +100°C for 24 hours.

Cells were discharged in order to determine an optimum cathode current density and thickness for a given fabrication density. Initial tests used cathodes containing 95% carbon black and 5% Teflon. Each cathode contained 0.10g of cathode mix. An excess of 1.5 M LiAlCl₄ electrolyte was used in all tests. The cells were discharged at +20°C using constant resistive loads of 60, 200, and 390 ohms. Figures 10, 11, and 12 show the resulting discharge curves. The cells discharged under a 60-ohm load produced an average matrix utilization of 0.22 AH/cm³. The cells discharged under a 200 ohm load produced a current density of 2.7 mA/cm² and produced an average matrix utilization of 0.35 AH/cm³. The cells discharged under a 390-ohm load produced a current density of 1.4 mA/cm² and produced an average matrix utilization of .50 AH/cm³. As the resistive load increased, the current density decreased and the matrix utilization improved. A performance summary of Figures 10, 11, and 12 are summarized in Table 7.

PRESSED-5%TFE-.05GM/SIDE-60 OHM

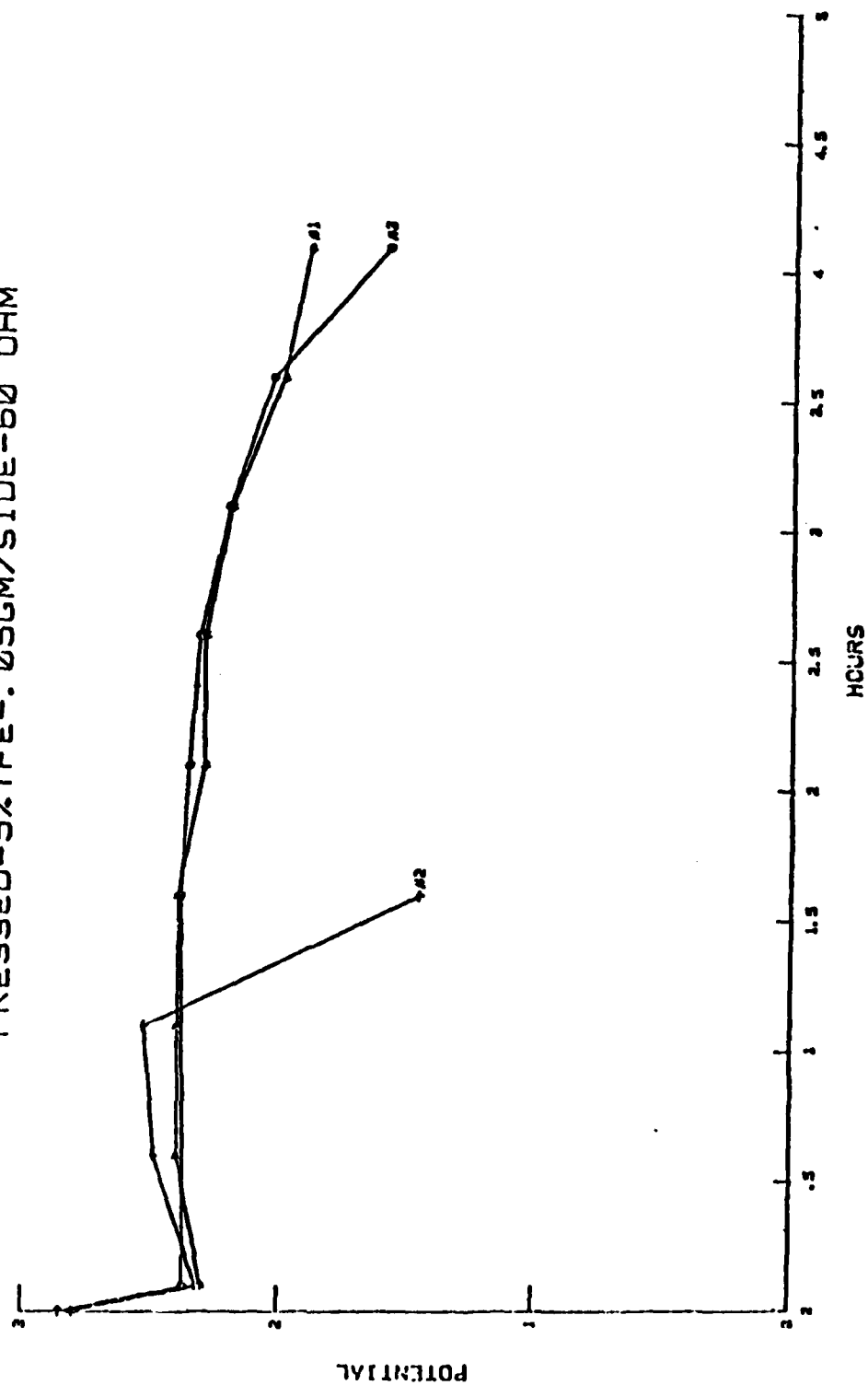


FIGURE 10 60 Ohm Discharges

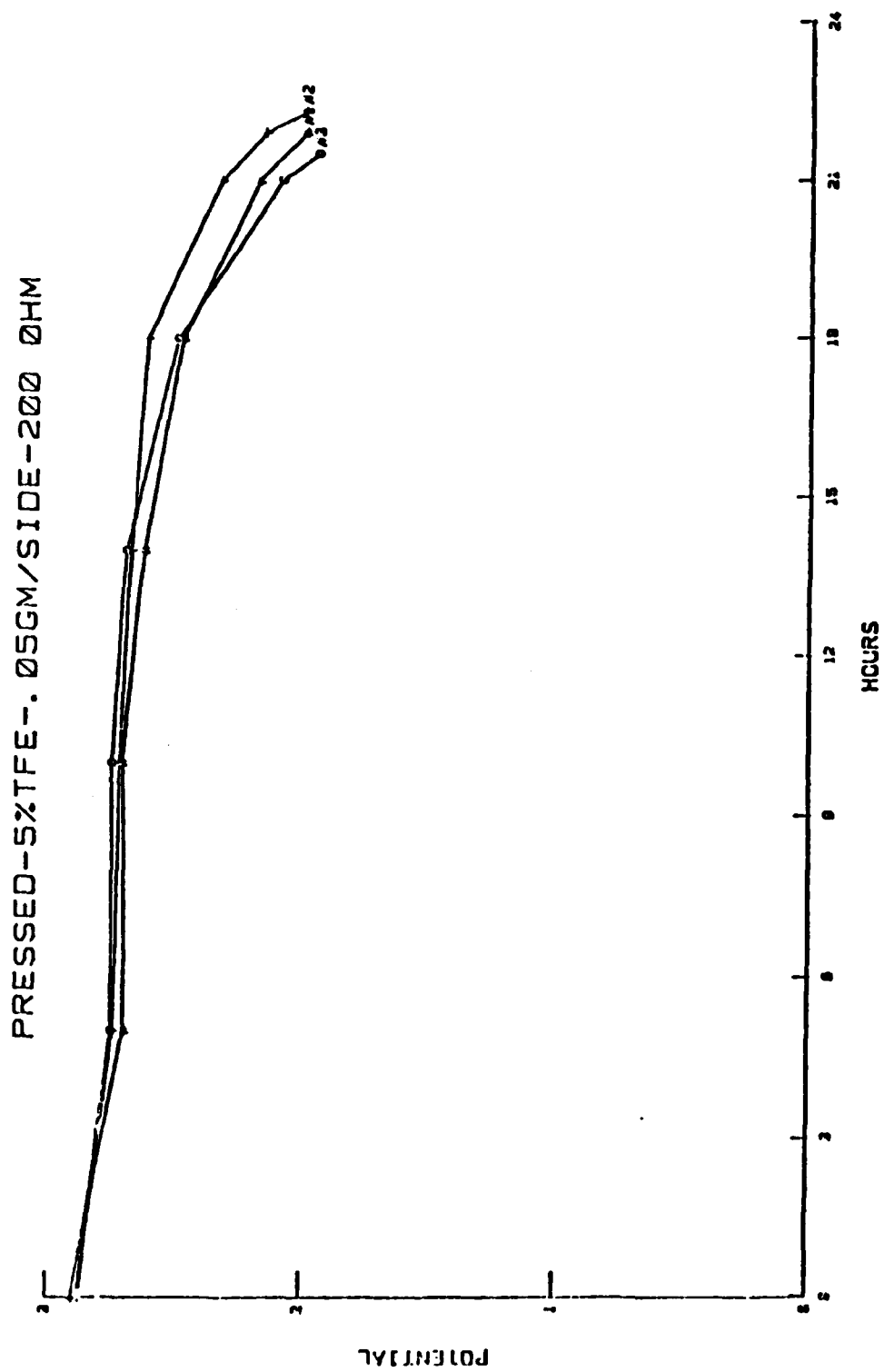


FIGURE 11 200 Ohm Discharges

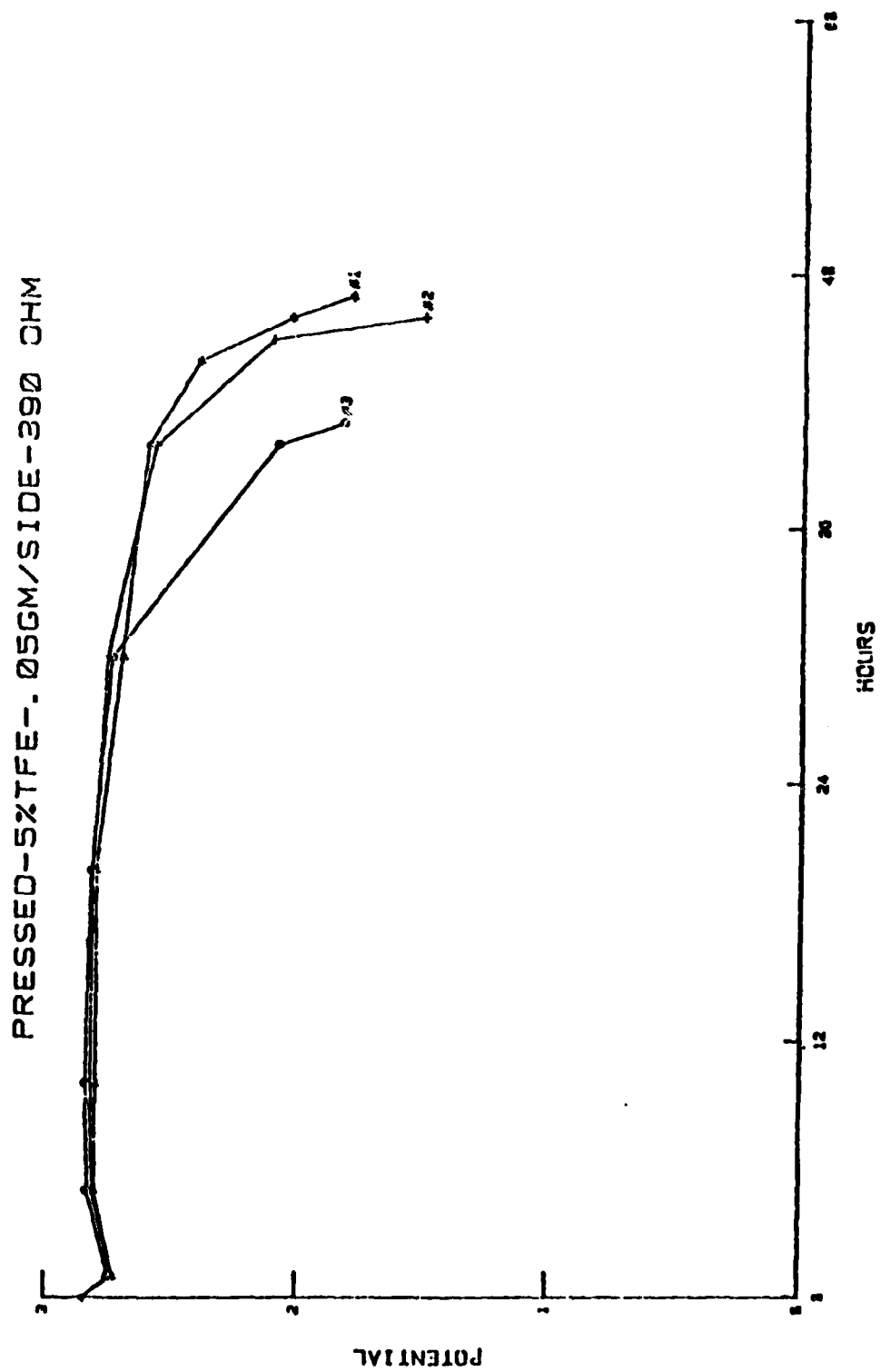


FIGURE 12 390 Ohm Discharges

TABLE 7 CATHODE PERFORMANCE

<u>Figure No.</u>	<u>Cathode</u>	<u>Load</u>	<u>Temp °C</u>	<u>AH to 2.0V</u>	<u>Ave.Pot</u>	<u>AH/cm³</u>	<u>AH/ GRAM</u>
10	95% C.Black,5% TFE, 0.10g	60	+20	0.167	2.320	0.22	1.37
11	95% C.Black,5% TFE, 0.10g	200	+20	0.217	2.620	0.35	2.17
12	95% C.Black,5% TFE, 0.10g	390	+20	0.308	2.720	0.50	3.08
13	95% C.Black,5% TFE, 0.20g	200	+20	0.331	2.605	0.39	1.66
14	95% C.Black,5% TFE, 0.20g	390	+20	0.386	2.762	0.46	1.93
15	90% C.Black,10% TFE, 0.10g	390	+20	0.346	2.521	0.46	3.46
16	97% C.Black, 3% TFE, 0.10g	390	+20	0.314	2.551	0.56	3.14
17	97% C.Black, 3% TFE, 0.10 g	390	+20	0.259	2.437	0.40	2.59

(sintered)

Additional cathode testing used cathodes containing 0.20 g of material instead of 0.10g. The cells were discharged under constant resistive loads of 200 and 390-ohms. Figures 13 and 14 show the resulting discharge curves. The cells discharged under 200-ohms produced an average matrix utilization of 0.39 AH/cm³. This matrix utilization was a slight improvement over the 0.10g cathode discharged under a 200-ohm load. The 0.20 g cathode discharged under a 390-ohm load produced a matrix utilization of 0.46 AH/cm³. This was a drop from the matrix utilization resulting from the cathodes weighing 0.10 g and discharged under a 390-ohm load. A performance summary of Figures 13 and 14 is given in Table 7.

All tests previously described contained 5% Teflon binder. Another group of cells were fabricated containing 3% or 10 Teflon binder. Each cathode contained 0.10 g of cathode mix. The cells were discharged under a 390-ohm load at +20°C. Figures 15 and 16 show the resulting discharge curves. Cell performance is summarized in Table 7. Table 7 shows that the cathodes containing 3% Teflon produced the highest matrix utilization, 0.56 AH/cm³, and a very high specific capacity, 3.14 AH/GM. However, the 3% Teflon cathodes had poor mechanical properties thus making handling difficult. While electrical performance of such cathodes was satisfactory, they were too delicate to be used in full size cell production.

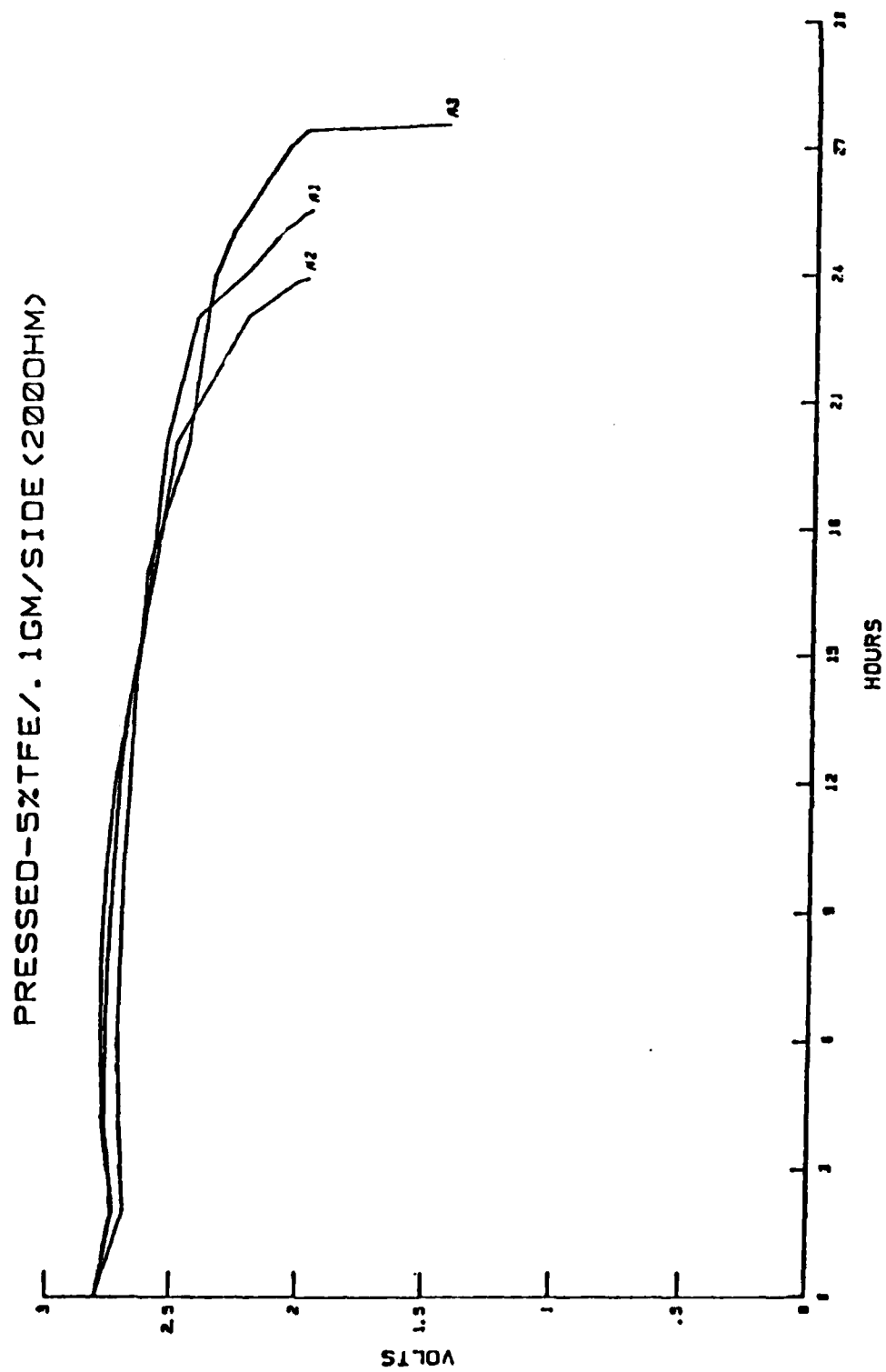


FIGURE 13 200 Ohm Discharges

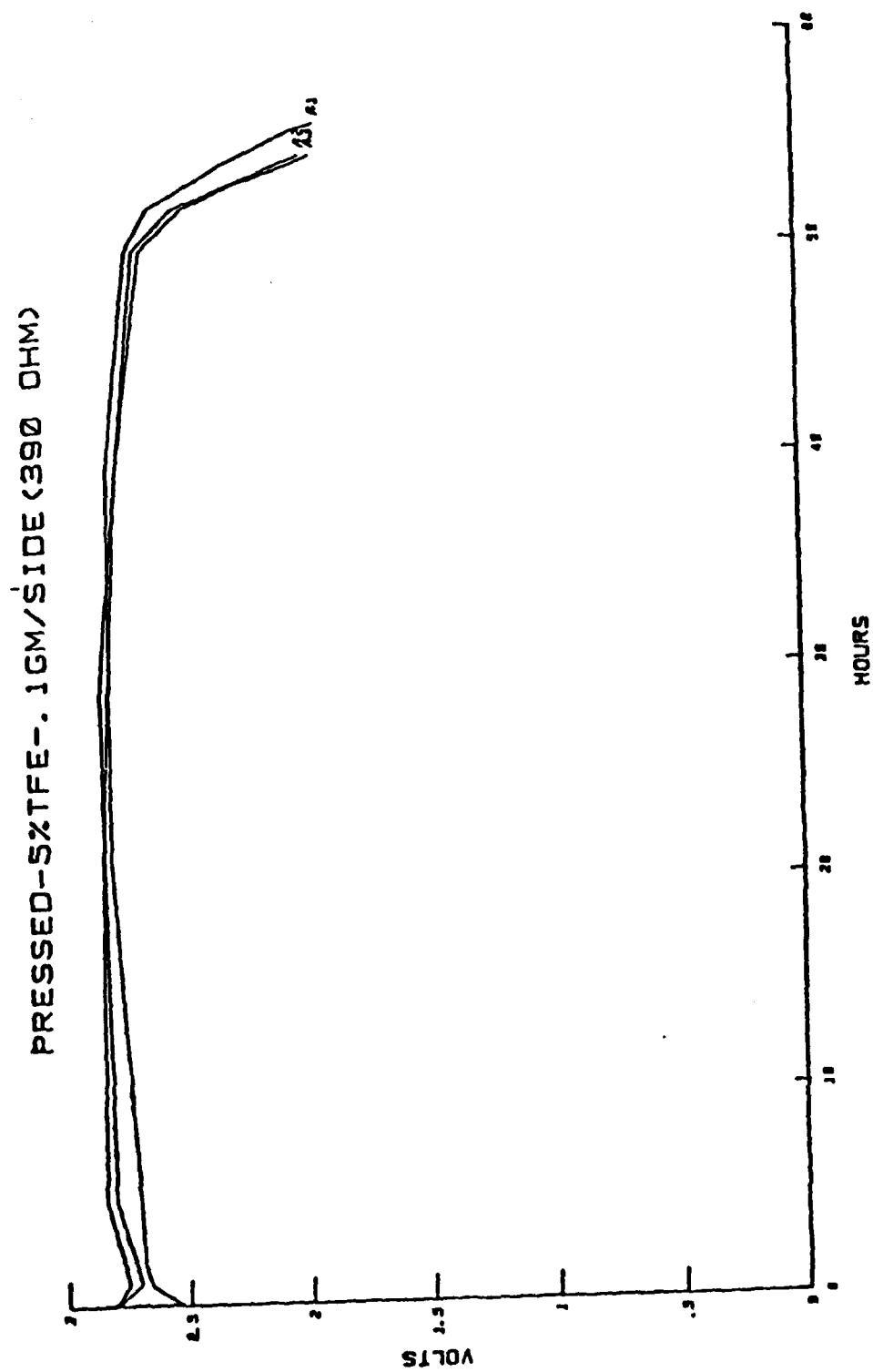


FIGURE 14 390 Ohm Discharges

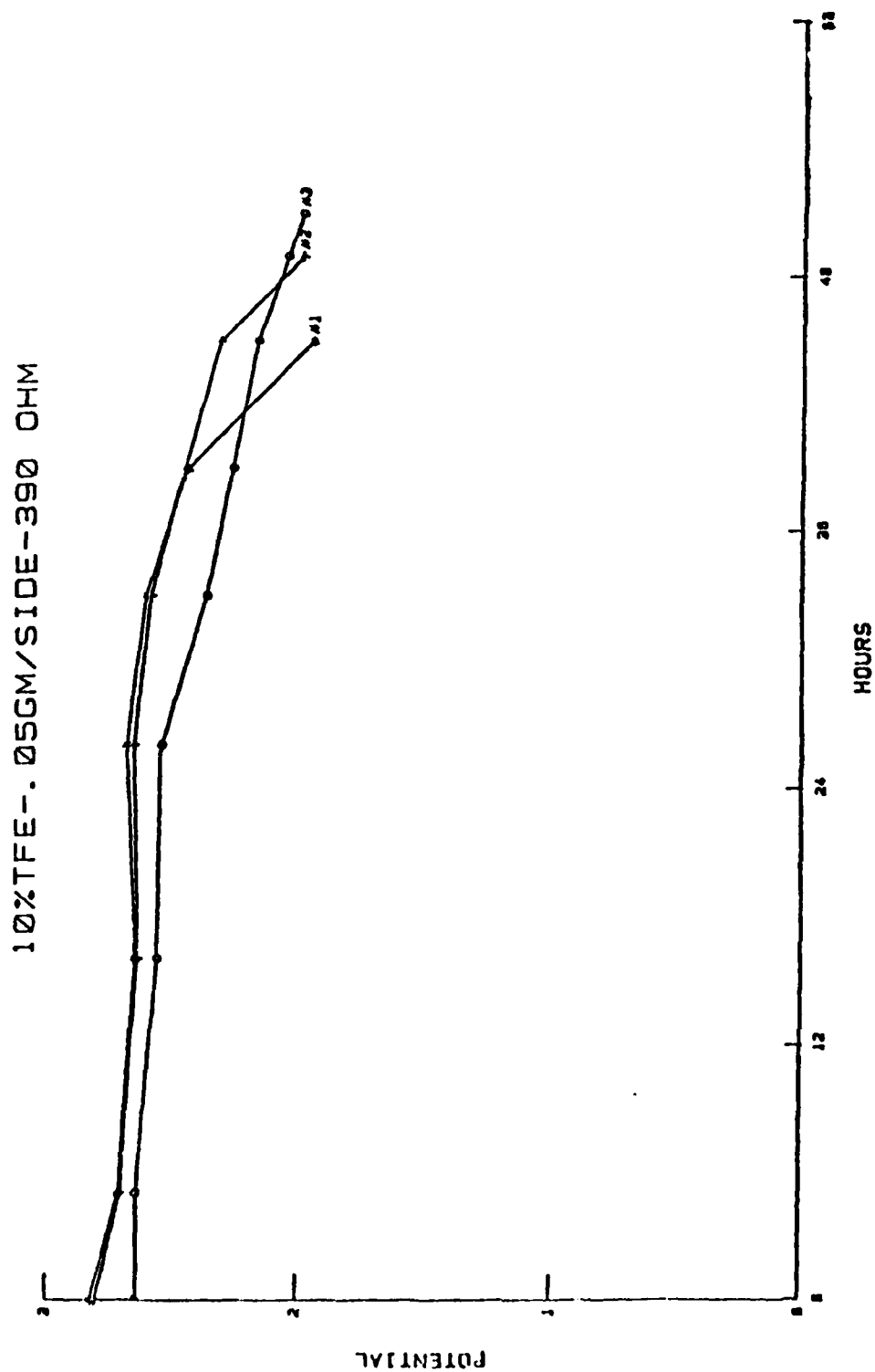


FIGURE 15 390 Ohm Discharges - 10% TFE

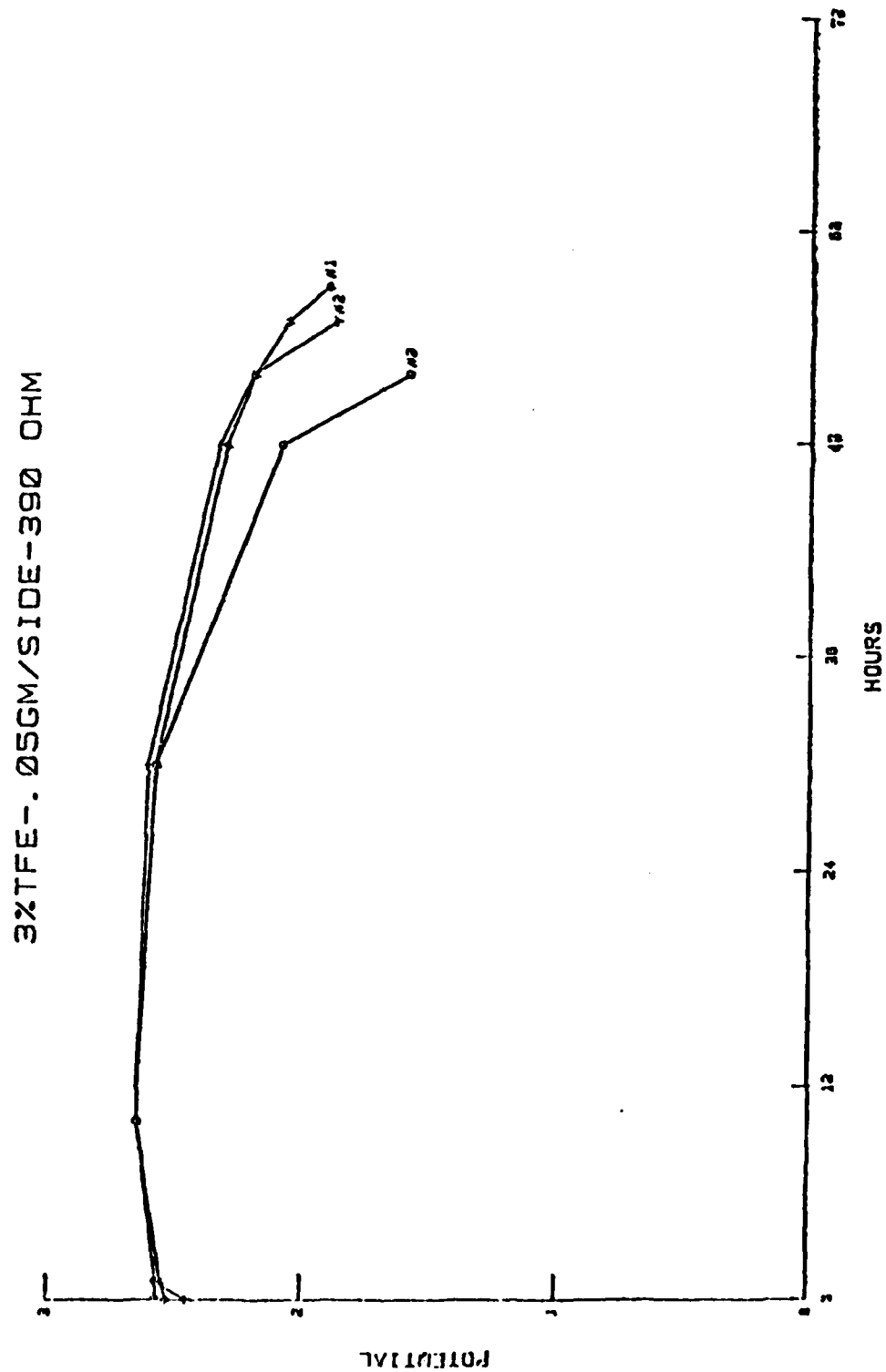


FIGURE 16 390 Ohm Discharges - 3% TFE

In order to improve the mechanical properties of 3% Teflon cathodes, cathodes were sintered at $+600^{\circ}\text{F}$ for 15 minutes. The baking process caused the Teflon binder to flow and mix more uniformly throughout the cathode thus resulting in a more strongly bound cathode. The performance of sintered 3% cathodes is summarized in Table 7. Table 7 shows overall electrical performance of the sintered cathodes was inferior to the 3% cathodes earlier tested. Mechanical properties, however, were improved following the sintering process.

Table 8 shows the maximum number cathodes which could be built into a 14-AH cell having a maximum volume of 3.2 in^3 , and a cathode capable of providing 0.50 AH/cm^3 . A cathode made from 0.10 g of mix containing 95% carbon black and 5% Teflon has a matrix utilization of 0.50 AH/cm^3 when discharged at 1.4 mA/cm^2 . Table 8 shows that a matrix utilization of 0.50 AH/cm^3 and current density of 1.4 mA/cm^2 requires that no less than 10 cathodes be built into the cell.

3.2 Cathode Density and Thickness Study

Tests optimizing cathode density and thickness simultaneously evaluated electrolyte formulation and concentration. Cathodes were fabricated in a Carver Laboratory Press at 250 psi ($.250\text{ g/cm}^3$) and 5000 psi ($.376\text{ g/cm}^3$). Those two pressures were chosen as the minimum and maximum pressures which were capable of giving consistent and easily reproducible cathodes. Cathodes were pressed in a machined die, the resultant cathode dimensions being $0.660'' \times 0.530''$. Cathode thicknesses studied were: $0.050''$, $0.100''$, $0.150''$, $0.200''$.

TABLE 8 - CELL DESIGN PRINTOUT

Utilization = 0.5
 Excess Calcium = 0.10
 Separator Thickness = 0.005

<u>Cathode Number</u>	<u>Cathode Thickness</u>	<u>Current Density</u>	<u>Anode Thickness</u>	<u>Total Separator</u>	<u>Total Thickness</u>
1	0.7397	13.4228	0.0991	0.0100	0.9480
2	0.3698	6.7114	0.0661	0.0200	0.9580
3	0.2466	4.4743	0.0496	0.0300	0.9680
4	0.1849	3.3557	0.0397	0.0400	0.9780
5	0.1479	2.6846	0.0330	0.0500	0.9880
6	0.1233	2.2371	0.0283	0.0600	0.9980
7	0.1057	1.9175	0.0248	0.0700	1.0080
8	0.0925	1.6779	0.0220	0.0800	1.0180
9	0.0822	1.4914	0.0198	0.0900	1.0280
10	0.0740	1.3423	0.0180	0.1000	1.0380
11	0.0672	1.2203	0.0165	0.1100	1.0480
12	CELL WIDTH EXCEEDS LIMITS				

Shawinigan carbon black 18.8 g + 1.2 g emulsified TFE-30 binder + 500 ml distilled water mixed in a blender and placed in a vacuum jig to remove excess water composed the cathode mix. The mixture was allowed to dry 48 hours in dry room atmosphere, then powdered in a blender. The amount of cathode mix was weighed and pressed to give the final cathode. Exmet 5Ni7-2/0 with Ni tab spot welded onto it was used as the cathode collector grid.

The actual testing of cathodes involved glass test cells with ground glass domed covers. Terminals passing through the sides of the cells allowed for an air tight seal when the cover was in place. The anodes consisted of 0.050" thick Pfizer Calcium slightly larger than the cathode. Each anode was scraped to expose shiny Ca and remove any oxide or corrosion layers. Ni tab was spot welded to the Ca. Dexter separator was cut and folded around each cathode. The cathode was then sandwiched between two Ca pieces and placed in the glass cell. A weight was placed on the Cathode/Anode sandwich to maintain even pressure. The Ni tabs were connected to the cell terminals with small alligator clips. Each cell was activated with 13-15 ml electrolyte. Cells were discharged at four different rates (30 mA/cm², 25mA/cm², 19 mA/cm², 16mA/cm²) for each thickness cathode (0.50", 0.100", 0.150", 0.200") at each cathode density (0.250 g/cm³ and 0.375 g/cm³). Three electrolyte concentrations were also studied simultaneously within the above matrix. As a result, 96 glass test cells (32/each electrolyte concentration) were discharged at room temperature, 20°C. See Table 9 for discharge data. The cathodes at 0.100" and 0.150" thickness gave the best performance. The only binder in the cathode was Teflon (TFE-30). Since excessive binder harms performance, 8% TFE concentration was chosen as the least amount needed to give consistent and easily reproducible cathodes. The 8% TFE concentration was determined by trial and error fabrication of cathodes.

3.3 Electrolyte Formulation and Concentration

During the program, substitutes for AlCl_3 and LiCl have been tried but AlCl_3 and LiCl have proven to give the best cell performance with Thionyl Chloride. Therefore, varying concentrations of AlCl_3 with LiCl in SOCl_2 were studied. The ratios of AlCl_3 to LiCl studied are as follows: 2 Molar:1 Molar 3 Molar:1 Molar 4 Molar:1 Molar. Note that the $\text{AlCl}_3/\text{LiCl}$ is not merely a ratio, but also designates concentration. The electrolyte solutions were prepared by dissolving the appropriate amount of Fluka AlCl_3 in Kodak SOCl_2 until completely dissolved then adding Fluka LiCl in the appropriate amount and stirring on a magnetic stirrer with stir bar. The electrolytes were evaluated simultaneously with the Cathode Thickness Density Study. See Table 9 for data. 3:1 electrolyte (3M AlCl_3 :1M LiCl) gave the best performance.

3.4 Cathode/Temperature Study

A temperature study was conducted at 38°C using glass test cells. After selecting an electrolyte (3:1) and eliminating all but the 0.100" and 0.150" thick cathodes with 8% TFE binder at 0.250 g/cm^3 and 0.375 g/cm^3 , the glass test cells were prepared as described in Section 3.2. Stainless steel vessels capable of withstanding extreme pressure were preheated in an oven to 38°C . Each vessel could hold one glass test cell. An uncovered glass test cell was placed in each vessel. The test cell was activated with a syringe through a removable fitting in the top of the S.S. vessel. Each vessel was insulated by pouring vermiculite around it immediately after activation with the 3:1 electrolyte. The S.S. vessel contained sufficient mass to act as a heat sink, so temperature fluctuation was minimal. See Table 10 for data.

TABLE 9: CATHODE MATRIX

CATHODE THICKNESS-DENSITY-ELECTROLYTE STUDY

mA/cm ²	V	Min. to 2.0 V	AH/cm ³	WH/cm ³	Thickness	Fabrication Pressure
30	2.04	5	.031	.063	.050	250
25	2.10	17	.090	.190	.050	250
19	2.17	37	.152	.330	.050	250
16	2.18	43	.147	.320	.050	250
30	2.05	10	.062	.130	.050	5000
25	2.13	17	.091	.190	.050	5000
19	2.24	55	.222	.500	.050	5000
16	2.27	48	.176	.400	.050	5000
30	2.13	46	.162	.350	.100	250
25	2.13	47	.138	.300	.100	250
19	2.28	98	.230	.520	.100	250
16	2.29	140	.274	.630	.100	250
30	2.08	20	.073	.150	.100	5000
25	2.18	54	.172	.370	.100	5000
19	2.34	116	.286	.670	.100	5000
16	2.31	125	.272	.630	.100	5000
30	2.12	51	.135	.290	.150	250
25	2.18	88	.199	.430	.150	250
19	2.26	197	.348	.790	.150	250
16	2.34	208	.315	.740	.150	250
30	2.08	35	.085	.180	.150	5000
25	2.19	75	.159	.350	.150	5000
19	2.25	133	.218	.490	.150	5000
16	2.35	171	.250	.590	.150	5000
30	2.14	75	.146	.310	.200	250
25	2.16	94	.154	.330	.200	250
19	2.25	182	.233	.520	.200	250
16	2.33	270	.295	.690	.200	250
30	2.07	20	.036	.075	.200	5000
25	2.19	96	.153	.340	.200	5000
19	2.32	150	.190	.440	.200	5000
16	2.15	195	.196	.420	.200	5000

Temperature - 20°C

Electrolyte - 2:1 AlCl₃/LiCl

TABLE 9: CATHODE MATRIX (Continues)

CATHODE THICKNESS-DENSITY-ELECTROLYTE STUDY

mA/cm ²	V	Min. to 2.0 V	AH/cm ³	WH/cm ³	Thickness	Fabrication Pressure
30	2.08	20	.124	.260	.050	250
25	2.13	45	.242	.520	.050	250
19	2.21	85	.302	.670	.050	250
16	2.14	95	.317	.680	.050	250
30	2.07	15	0	0	.050	5000
25	2.09	31	.164	.340	.050	5000
19	2.27	75	.322	.730	.050	5000
16	2.27	119	.423	.960	.050	5000
30	2.20	50	.002	.004	.100	250
25	2.17	90	.270	.580	.100	250
19	2.15	80	.180	.380	.100	250
16	2.29	175	.330	.750	.100	250
30	2.07	30	.110	.230	.100	5000
25	2.17	65	.210	.450	.100	5000
19	2.27	135	.340	.770	.100	5000
16	2.33	175	.370	.870	.100	5000
30	2.15	36	.089	.200	.150	250
25	2.18	35	.074	.160	.150	250
19	2.24	125	.203	.450	.150	250
16	2.33	210	.295	.690	.150	250
30	2.15	60	.150	.320	.150	5000
25	2.23	87	.190	.420	.150	5000
19	2.28	160	.270	.600	.150	5000
16	2.37	230	.330	.780	.150	5000
30	2.15	26	.049	.100	.200	250
25	2.16	75	.120	.250	.200	250
19	2.23	135	.160	.360	.200	250
16	2.35	226	.240	.560	.200	250
30	2.13	12	.021	.050	.200	5000
25	2.24	70	.110	.250	.200	5000
19	2.28	235	.280	.640	.200	5000
16	2.36	248	.260	.620	.200	5000

Temperature - 20°C

Electrolyte - 3:1 AlCl₃/LiCl

TABLE 9: CATHODE MATRIX (Concluded)

CATHODE THICKNESS-DENSITY-ELECTROLYTE STUDY

mA/cm ²	V	Min. to 2.0 V	AH/cm ³	WH/cm ³	Thickness	Fabrication Pressure
30	-	-	-	-	.050	250
25	2.05	10	.051	.100	.050	250
19	2.15	25	.103	.220	.050	250
16	2.13	75	.25	.530	.050	250
30	-	-	-	-	.050	5000
25	-	-	-	-	.050	5000
19	2.11	15	.064	.130	.050	5000
16	2.19	132	.280	.610	.050	5000
30	2.00	4	.010	.021	.100	250
25	2.18	45	.133	.290	.100	250
19	2.25	130	.303	.680	.100	250
16	2.28	150	.292	.670	.100	250
30	2.12	4	.015	.031	.100	5000
25	2.12	17	.052	.110	.100	5000
19	2.13	105	.240	.520	.100	5000
16	2.18	120	.240	.520	.100	5000
30	2.04	4	.010	.020	.150	250
25	2.09	30	.062	.130	.150	250
19	2.16	76	.120	.260	.150	250
16	2.19	151	.201	.440	.150	250
30	2.08	4	.009	.020	.150	5000
25	2.13	40	.007	.160	.150	5000
19	2.19	151	.230	.490	.150	5000
16	2.27	210	.270	.610	.150	5000
30	2.00	2.5	.004	.010	.200	250
25	2.15	45	.059	.130	.200	250
19	2.17	105	.108	.230	.200	250
16	2.17	150	.123	.270	.200	250
30	2.07	8	.014	.029	.200	5000
25	2.15	65	.097	.210	.200	5000
19	2.23	105	.120	.120	.200	5000
16	2.24	232	.220	.220	.200	5000

Temperature - 20°C

Electrolyte - 4:1 AlCl₃/LiCl

TABLE 10
CATHODE/TEMPERATURE STUDY

mA/cm ²	V	Min. to 2.0 V	AH/cm ³	WH/cm ³	Thickness	Fabricated Pressure
30	2.35	49	.242	.587	0.100	5000
25	2.18	70	.304	.714	0.100	5000
19	2.33	120	.289	.778	0.100	5000
16	2.60	.42	.308	.804	0.100	5000
30	2.42	57	.139	.327	0.150	5000
25	2.56	80	.154	.336	0.150	5000
19	2.47	112	.210	.489	0.150	5000
16	2.61	126	.23	.621	0.150	5000
30	2.41	52	.228	.549	0.100	250
25					0.100	250
19	2.46	96	.212	.669	0.100	250
16	2.54	165	.354	.899	0.100	250
30					0.150	250
25	2.43	110	.266	.646	0.150	250
19	2.40	117	.203	.487	0.150	250
10	2.47	156	.237	.585	0.150	250

Temperature - 38°C
Electrolyte - 3:1 AlCl₃/LiCl

The following test criteria were determined to provide the best performance: 1) Cathode thickness of 0.100" 2) The higher density cathode, 0.375 g/cm³ 3) Electrolyte containing 3 M AlCl₃/1 M LiCl/50Cl₂ 4) 8% TFE binder.

3.5 Cathode Enhancement Additives

Cathode additives studied were: Cobalt Phthalocyanine (Co Phth) and Iron Phthalocyanine (Fe Phth.). Other additives considered were: Calcium Propionate, Magnesium Chloride. The latter two failed to make a structurally sound cathode at the 10% level and were rejected for further consideration.

Co Phth. and Fe Phth. were added to the standard cathode mix (8% TFE, 92% carbon black). Levels studied were: 10%, 20%, 50%. The 50% level of both additives posed problems when pressing the cathodes. They tended to stick to the die and failed to bind acceptably.

Glass test cells with a cathode size of 0.660" x .530" x 0.100" thick, Dexter 255 separator and .050" thick Ca anodes were activated at 20°C with 3:1 electrolyte. All cathodes were fabricated at 5000 psi with resulting densities varying with the type and amount of additive. Current densities used were: 30 mA/cm², 25 mA/cm², 19 mA/cm², 16 mA/cm². See Table 11 for glass test cell results.

The additive Co Phth outperformed Fe Phth, so Co Phth was evaluated further in full-sized cells. The 20% and 50% levels of Co Phth hindered cell performance. BCl₃ was also evaluated as a cathode additive. It outperformed either Fe CoPh or Co Phth., but the glass test cells showed continuous gassing after activation, so BCl₃ was dropped from further consideration. The 10, 20 and 50% levels referred to for BCl₃ were for a 1.0M

mixture of BCl_3 in hexane, added to 3:1 electrolyte on a volume basis. See Table 11 for glass test cell data on the additives. BI_3 was also considered as an additive, but proved to react quite violently with thionyl chloride.

TABLE 11
CATHODE ADDITIVES

mA/cm^2	V	Min to 2.0 V	AH/cm^3	WH/cm^3	Additive
30	2.20	60	.233	.513	10% BCl_3
30	2.32	26	.102	.237	20% BCl_3
30	2.24	9	.034	.076	50% BCl_3
30	2.20	60	.233	.513	10% BCl_3
25	2.17	56	.178	.386	10% BCl_3
19	2.33	106	.262	.610	10% BCl_3
16	2.31	134	.283	.654	10% BCl_3
30	2.11	54	.206	.435	10% CoPh
30	2.17	29	.126	.273	20% CoPh
30	2.16	14	.068	.147	50% CoPh
30	2.24	42	.173	.387	10% FePh
30	2.17	28	.108	.234	20% FePh
30	2.14	14	.061	.231	50% FePh

Temp. of discharge - 20°C

Cathode Thickness - .100 inch

Electrolyte used 3:1 $\text{AlCl}_3/\text{LiCl}$

Cathode Fabrication Pressure - 5000 psi

SECTION IV

INITIAL RESERVE CELLS

4.1 Initial Full-Sized Cell Work

Two sizes of stainless steel rectangular cells were used for initial attempts at a full cell package. One was a Square-D cell of 3.2 in³ volume. The other was a rectangular (Rectcell) of 7.5 in³ volume.

Cell building was complicated by the brittleness and shock sensitivity of the large cathodes. The cathodes could not tolerate much handling. The structural integrity of the cathodes could be greatly improved by baking the cathode at 620⁰F for 30 minutes after the wet paste had dried 48 hours, but only at the expense of significant performance losses. The problem of grid separation was alleviated by increasing the TFE binder level from 8% to 10%. Cathode integrity was increased with little or no performance loss.

D-cells and Rectcells were assembled according to the following initial configuration:

	<u>D-Cell</u>	<u>Rectcell</u>
Cathode Quantity	8	7
Cathode size	1" x 1.875" x .100"	2.125" x 2.250" x .100"
Cathode binder	10% TFE	10% TFE
Anode quantity	9	8
Separator	Dexter 255	Dexter 255
Electrolyte	3:1	3:1
Electrolyte Volume	44 ml	72 ml

Figure 17 shows the discharge curve for an initial run with the D-cell. Temperature curves "e" and "f" are data from thermocouples attached to the cell at faces parallel and perpendicular to the cell stack, respectively. This and other initial cells were manually activated after a vacuum had been pulled on the cells. After activation, the metallic fill tubes were crimped for closure, which proved to be a less than reliable method. With none of the cells could a hermetic seal be assumed.

Figure 18 shows the discharge curve for an initial run with the 7.5 in³ Rectcell. The accompanying Table 12 shows cell data and a summary of discharge results. At about 12 minutes into the discharge, gassing from the cell became readily visible. Cell gassing is a problem which manifested itself in the larger cells but which was not apparent in the glass test cell work.

It had been assumed that a tight cell stack would maximize cell energy density without sacrifice of cell performance. A small test matrix was set up to test the theory. Duplicate Rectcells were assembled with the only difference being the elimination of a cathode in one of the cells. See Figures 19-21, with accompanying data Tables 13-15, for discharge curves and data summaries.

Comparison of the data for Figures 18-21 shows that full stack (7 cathode) cells, when insulated to prevent most outside heater transfer, performed comparatively poorly when compared with corresponding 6-cathode insulated cells. Unfortunately, no uninsulated 7-cathode cells were discharged for comparison. In comparing the data for insulated versus uninsulated 6-cathode cells, little performance difference can be noted, though not unexpectedly, the ultimate temperatures reached were less for

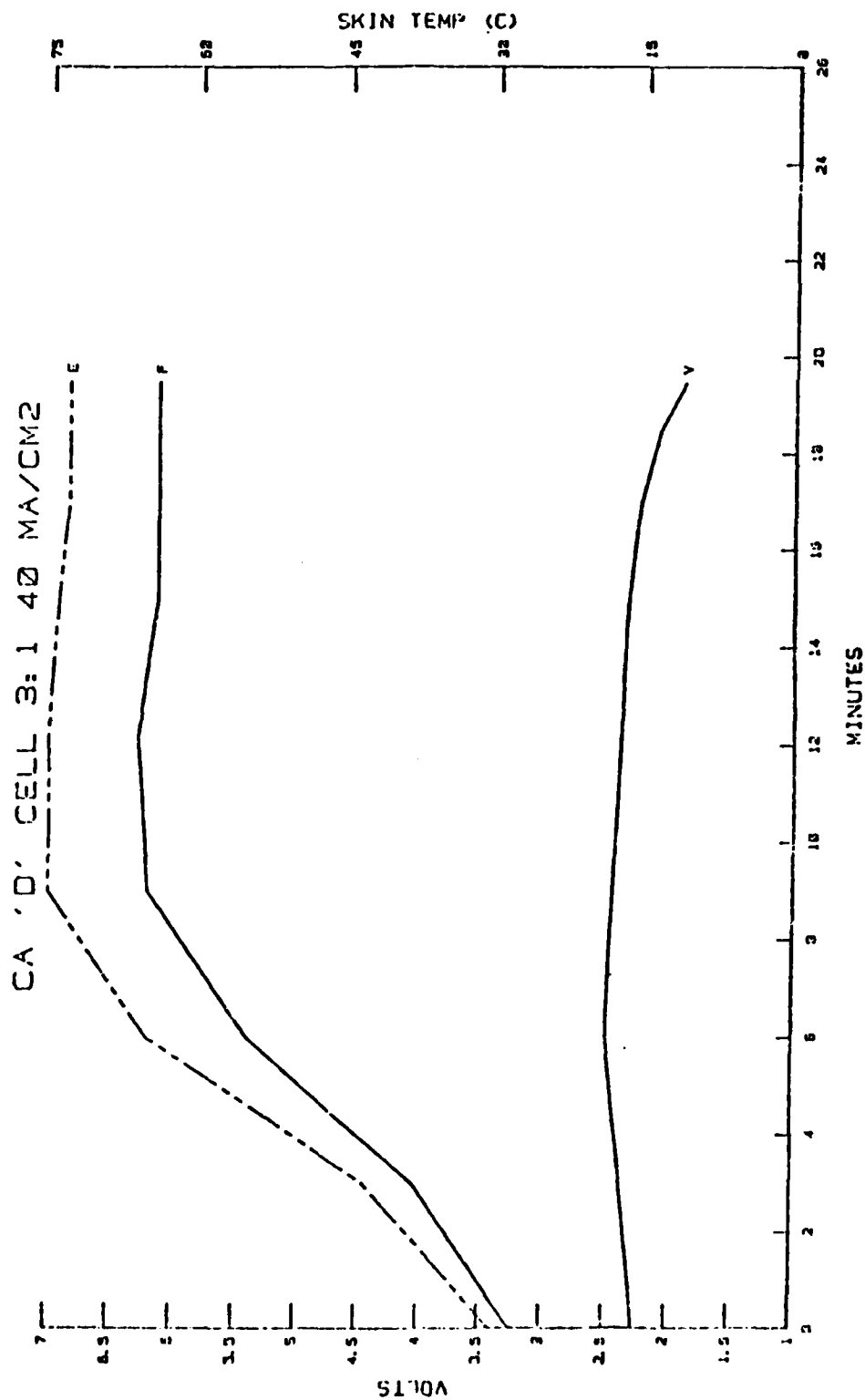


FIGURE 17 Initial D - Cell Discharge

TABLE 12 - FIGURE 18 CELL DATA

Insulated S.S. 7.5in³ Rectangular Cells

Cathodes - Seven

Cathode Composition - 8% TFE, unbaked, pressed

at 1500 psi, 2" x 1 7/8" x .100"

Electrolyte - 3:1 AlCl₃:LiCl

Load - .52 ohm

Discharge Data*

* Load applied ten minutes after activation

Average Potential - 2.14

VHr - 32.08

AmpHr - 1.03

Cathode Utilization - 0.024 AH/cm³

Cathode Volume - 43.0 cm³

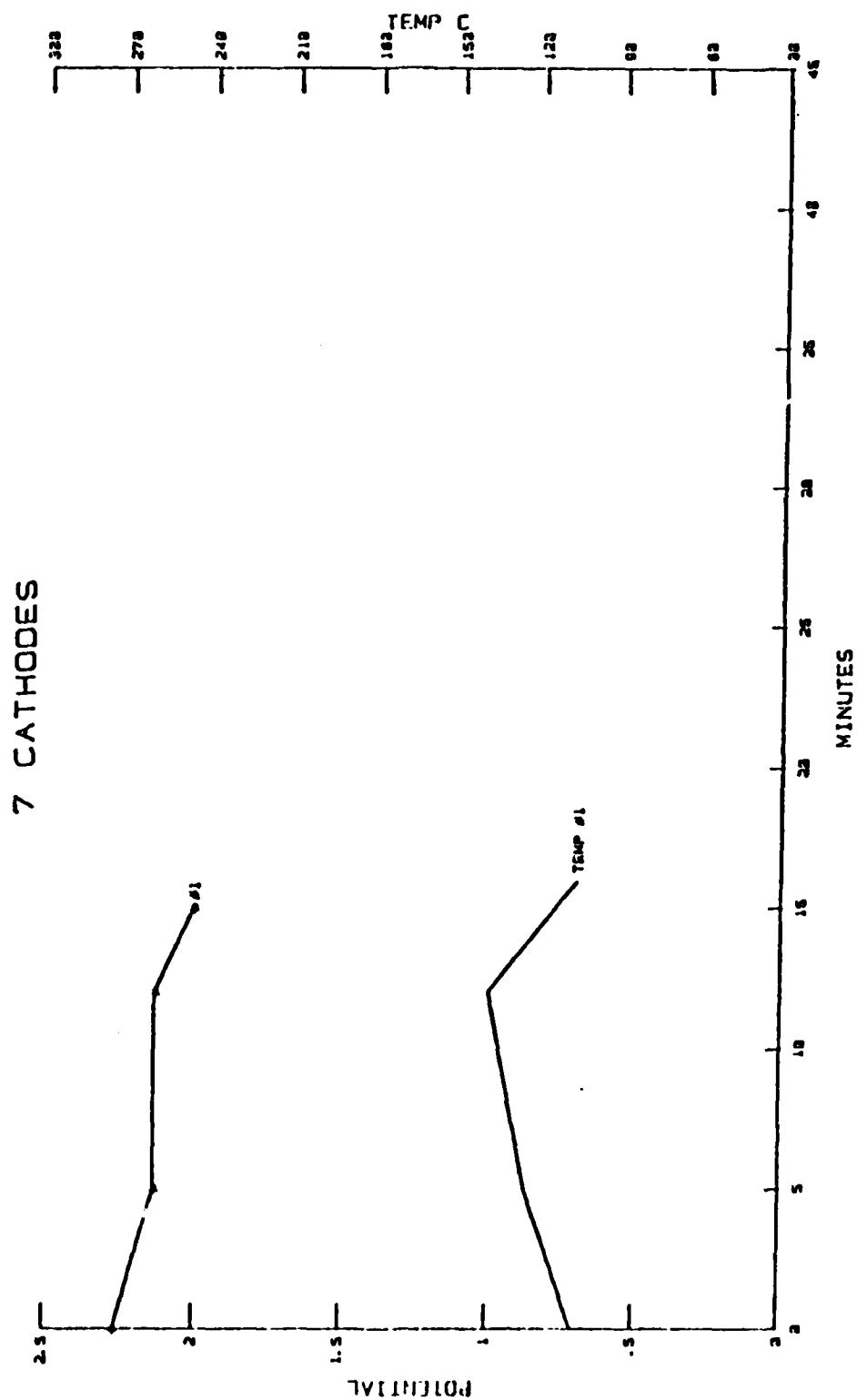


FIGURE 18 Initial Rectcell Discharge

TABLE 13 - FIGURE 19 CELL DATA
7.5 in³ S.S. Rectangular Cells

	<u>Cell #1</u>	<u>Cell #2</u>
Cell Insulation	Yes	Yes
No. of Cathodes	7	7
Cathode Size	2 1/8" x 2 1/4" x .090"	2 1/8" x 2 1/4" x .090"
Cathode Composition	10% TFE, unbaked pressed at 1000 psi	10% TFE, unbaked pressed at 1000 psi w/10% CoPhth
Electrolyte	3:1 AlCl ₃ :LiCl	3:1 AlCl ₃ :LiCl
Load	.48 ohm	.53 ohm

Discharge Data*

	<u>Curve #1</u>	<u>Curve #2</u>
v, avg.	2.12	2.15
VHr	29.7	85.9
AHr	1.03	2.7
Cathode Utilization	.021 AH/cm ³	.055 AHr/cm ³
Cathode Volume	49.3 cm ³	49.3 cm ³

* Cells were placed under load 10 minutes after activation

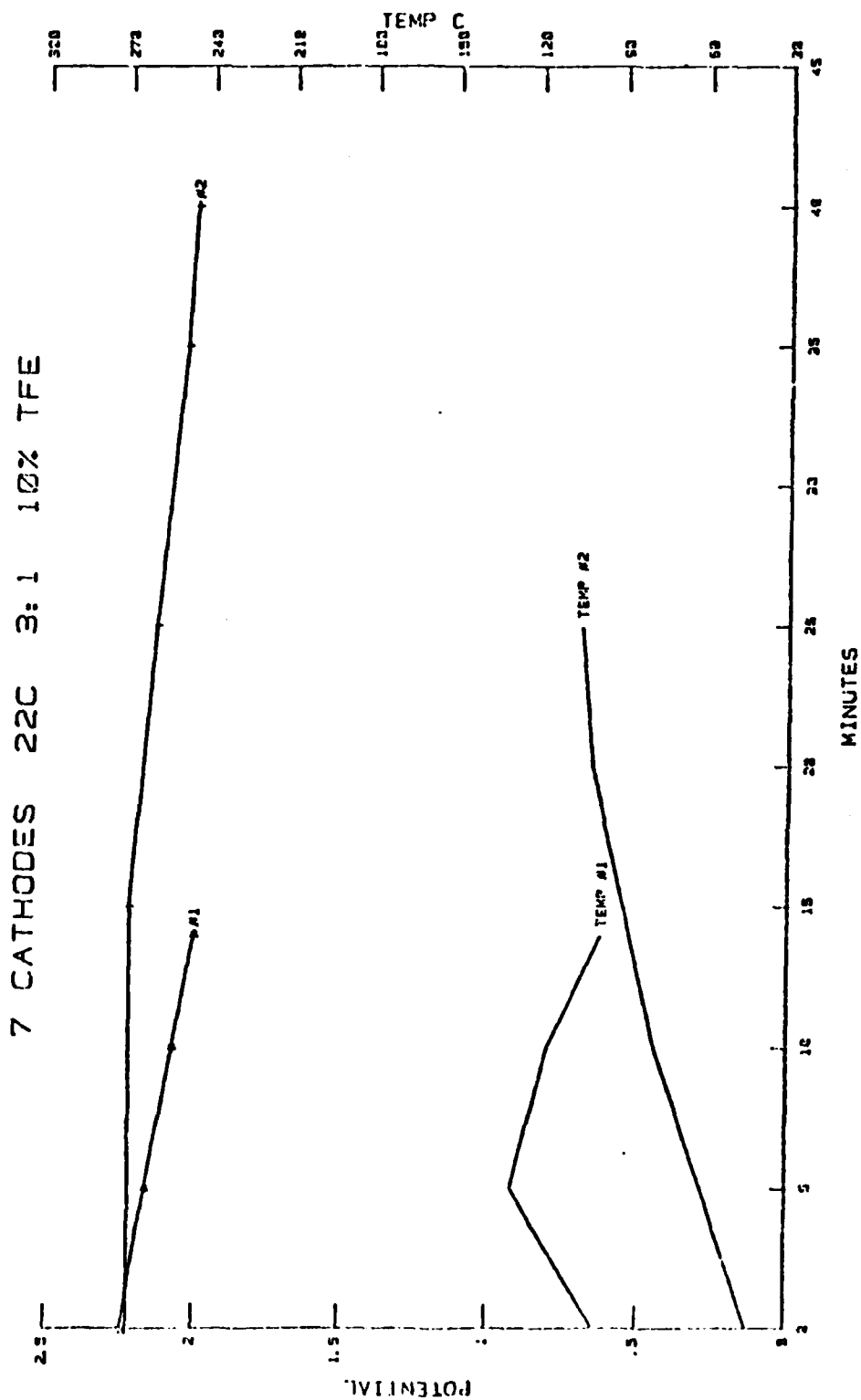


FIGURE 19 Cathode Additive Discharge Comparison

TABLE 14 - FIGURE 20 CELL DATA

7.5in³ S.S. Rectangular Cells

	<u>Curve #1</u>	<u>Curve #2</u>
Cell insulation	Yes	No
No. of cathodes	7	6
Cathode size	2 1/8" x 2 1/4" x .090"	2 1/8" x 2 1/4" x .090"
Cathode composition	10% TFE, unbaked pressed at 1000 psi 2/ 10% CoPhth	5% TFE, baked pressed at 1500 psi
Electrolyte	3:1 AlCl ₃ :LiCl	3:1 AlCl ₃ : LiCl
Load	.53 ohm	.52 ohm

Discharge Data*

	<u>Curve #1</u>	<u>Curve #2</u>
V, avg.	2.15	2.11
VHr	56.0	73.8
AHr	2.71	2.37
Cathode utilization	.055 AHr/cm ³	.056 AHr/cm ³
Cathode volume	49.3 cm ³	42.3 cm ³

* Cells were placed under load 10 minutes after activation

7 VS 6 CATHODES 22C 3:1

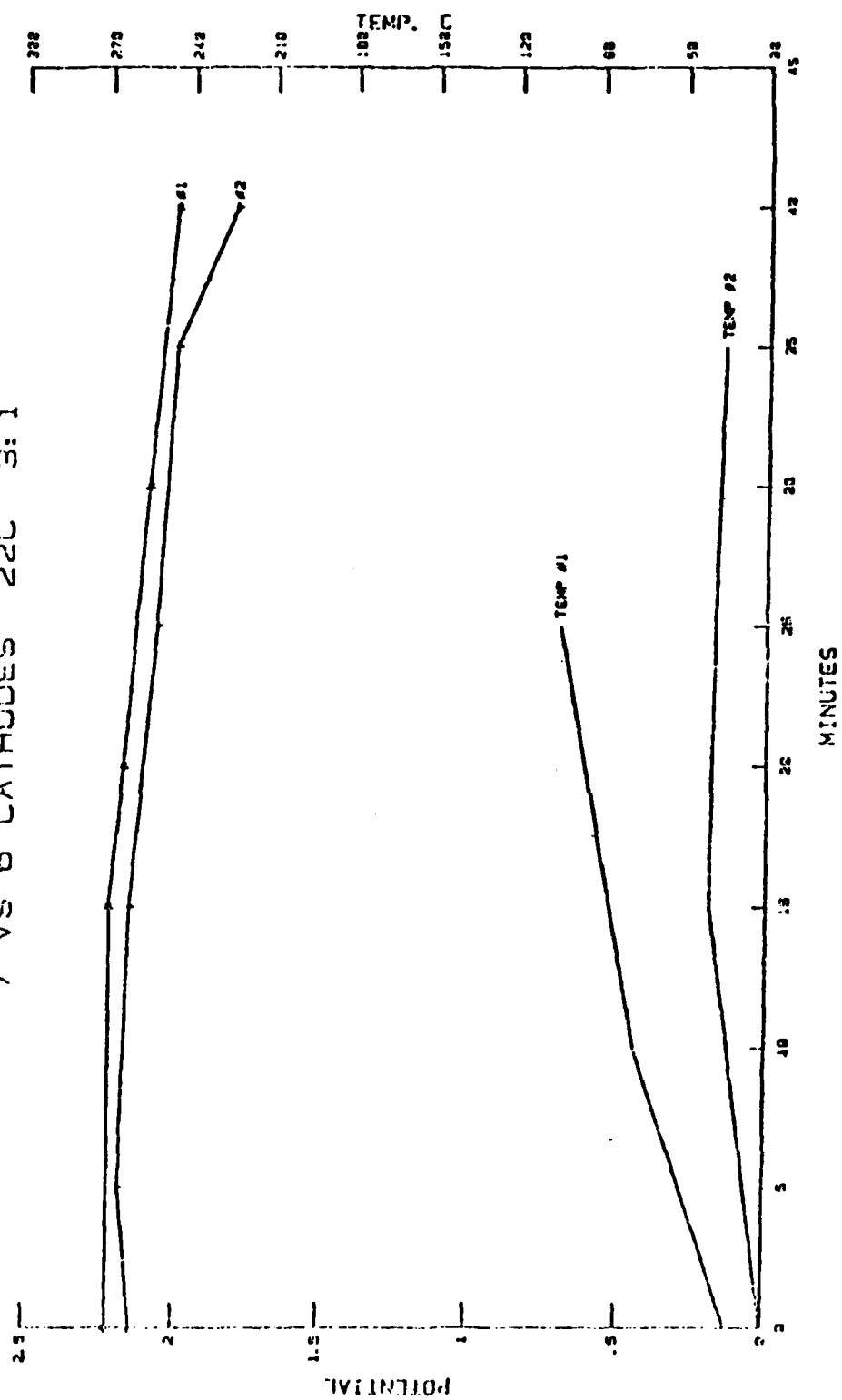


FIGURE 20 Tight VS Loose Stack Discharge

TABLE 15 - FIGURE 21 CELL DATA
7.5 in³ S.S. Rectangular Cells

	<u>Cell #1</u>	<u>Cell #2</u>
Cell insulation	No	Yes
No. of cathodes	6	6
Cathode size	2 1/8" x 2 1/4" x .090"	2 1/8" x 2 1/4" x .090"
Cathode composition	5% TFE, baked pressed at 1500 psi	10% TFE, unbaked pressed at 1000 psi
Electrolyte	3:1 AlCl ₃ :LiCl	3:1 AlCl ₃ :LiCl
Load	.52 ohm	.55 ohm

Discharge Data*

	<u>Curve #1</u>	<u>Curve #2</u>
V, avg.	2.11	2.19
VHr	73.8	76.55
AHr	2.36	2.32
Cathode Utilization	.056 AHr/cm ³	.055 AHr/cm ³
Cathode volume	42.3 cm ³	42.3 cm ³

* Cells were placed under load 10 minutes after activation

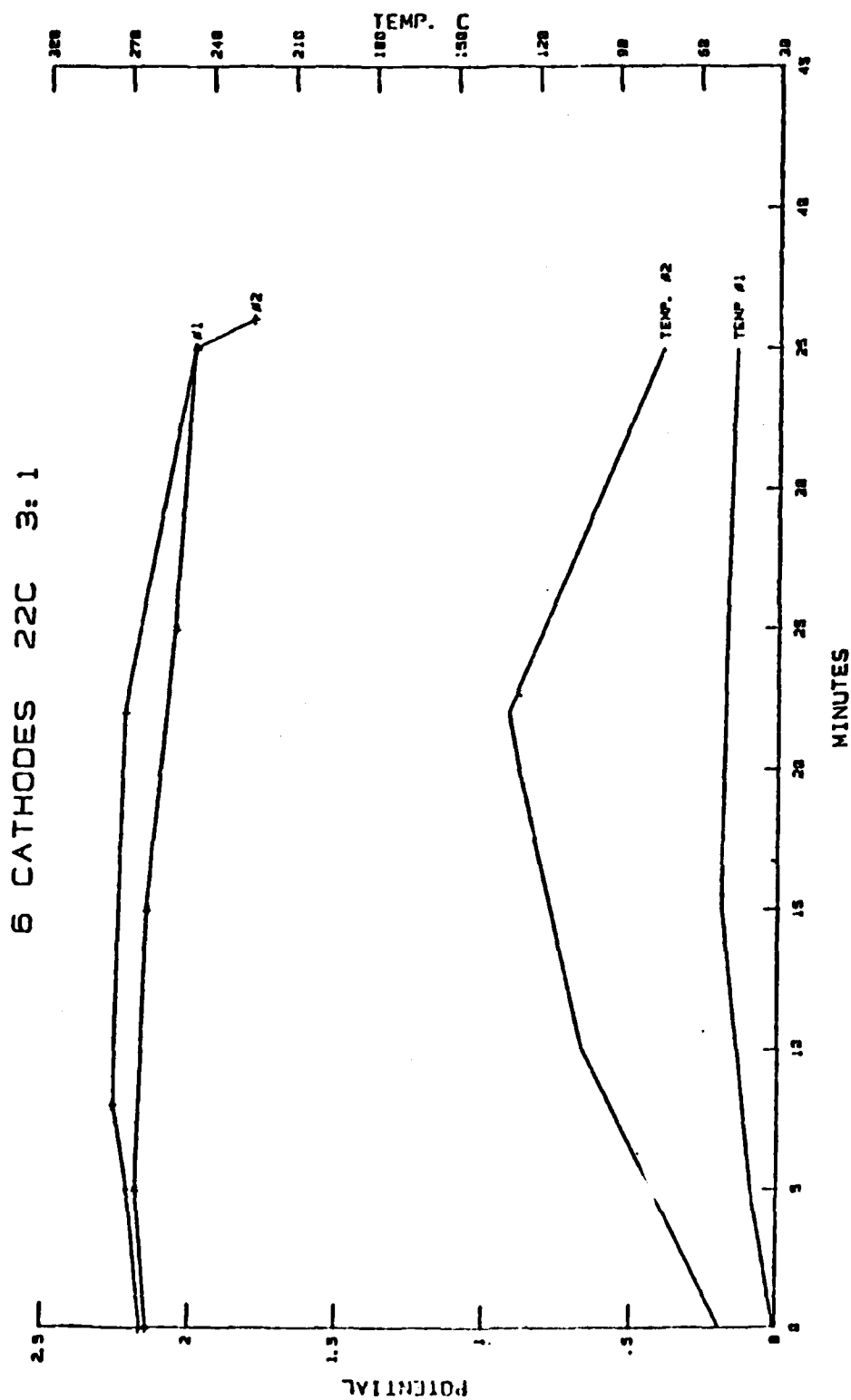


FIGURE 21 Insulated vs. Uninsulated Discharge

the uninsulated cells.

Cobalt Phtuhalocyanine was doped at the 10% level in the cathodes of Cell #2, Figure 19, and Cell #1, Figure 20. Both of these cells were insulated, 7-cathode cells. Comparison with the cell from Figure 18 and Cell #1 from Figure 19, shows a more rapid temperature rise for the cells without CoPhth. doping, coupled with a far slower voltage drop for the Co Phth doped cells. Comparison of Cell #2 from Figure 21 with Cell #1 from Figure 20 shows little temperature or performance difference between the 7-cathode cell doped with Co Phth, and the 6-cathode insulated cell.

A factor that renders the above comparisons suspect is that all the cells were outgassing from the crimped fill tubes to one degree or another. Hence, falling voltages may reflect significant electrolyte loss rather than cell depletion.

SECTION V

2ND PHASE ACTIVE CELL ELECTROLYTE INVESTIGATION

5.1 Screening - Calcium Salts

Any compound containing Calcium that was commercially available was initially considered a candidate as an electrolyte salt. Preliminary screening of each salt first involved a compatibility test between the salt and thionyl chloride. Each salt was combined with thionyl chloride at 20C. The test was performed in a moisture free glove box. The materials tested were considered compatible if there was no reaction producing gas-sing, precipitate, and/or color change. In some cases, the materials tested produced no obvious reactions and were insoluble in thionyl chloride. In other cases, the materials tested were soluble in thionyl chloride and showed no evidence of reacting with the solvent. Table 16 lists the materials evaluated and the compatibility with thionyl chloride. The salts which were found to be both insoluble and inert in thionyl chloride were considered to be a poor electrolyte salt, not worthy of further investigation. The compounds that were soluble or reactive with the solvent were considered to be potential electrolyte salts. In the case of a reaction between the salt and solvent, the reaction products were considered to contain electrolyte salts, expecially in cases where there were no precipitates formed. The compounds which were soluble in, or reacted with, thionyl chloride were further evaluated in ampule storage tests and electrical performance tests in .15 in³ stainless steel cells.

5.2 Screening - Solvents

Difficulty in finding Calcium salts compatible and/or soluble in

TABLE 16 - CALCIUM SALT - SOCl_2 COMPATIBILITY

<u>Ca-SALT</u>	<u>SOLUBLE/REACTIVE</u>	<u>INSOLUBLE/INERT</u>
- Acetate		X
- Acrylate		X
- Benzene Sulfonate		X
- Benzoate	X	
- Benzylphthalate		X
- Butyrate	X	
- Caproate	X	
- Caseinate		X
- Cyclamate		X
- Formate		X
- Gluconate		X
- Glutamate		X
- Glycerate		X
- Heptate	X	
- Hypochlorite	X	
- Lactobionate		X
- Laurate	X	
- Leuvinlate		X
- Malonate		X
- Mandelate		X
- Naphenate	X	
- Nucleate		X
- Octoate		X
- Oleate	X	
- Resinate	X	
- Salicylate	X	

TABLE 16 - CALCIUM SALT - SOCl_2 COMPATIBILITY
(Continued)

<u>Ca-SALT</u>	<u>SOLUBLE/REACTIVE</u>	<u>INSOLUBLE/INERT</u>
- Succinate		X
- Sulfamate		X
- Tartanate	X	
- Thioglycolate	X	
- Zirconate		X

thionyl chloride lead to a search for solvents to replace and/or help thionyl chloride dissolve salts readily. Solvents which met these conditions are referred to as Aprotics. Aprotic solvents have the ability to bring solute (Ca Salt) - solvent (thionyl chloride) together into solution. This arrangement allowed dissolution of many otherwise insoluble Calcium salts into thionyl chloride up to 1.0 Molar concentrations and beyond. See Table 17 for a list of all aprotic solvents screened. Only those salts of significant solubility were chosen to make ampules from subsequent glass test cells were prepared based on the ampule data. Table 18 is a list of Calcium Salts/Aprotics Compatibility.

5.3 Ampule - Storability/Compatibility

Sealed glass ampules were stored in an oven at 60C. Calcium salts and substitutes with thionyl chloride and Ca metal were observed for Ca corrosion, color change, and/or precipitate formation. See Table 19. Ampules containing Aprotic solvents with thionyl chloride and Ca metal were observed in the same manner. See Table 20. Observations on storage ampules with combinations of Calcium salts/Thionyl chloride/Aprotic solvents may be found in Table 21. Some of the aprotic solvents were responsible for ampule explosions and, in some cases, fire due to low flash points and low boiling points.

Solvents investigated as replacements for Thionyl Chloride and/or inhibitors were also stored in ampules and observed in glass test cells. See Table 22. The choice of many of these solvent/inhibitors was related to a functional group which resembled Thionyl Chloride. These functional groups included acetyl ($\overset{\text{Cl}}{\underset{\text{O}}{\text{C}}}=\text{O}$) and sulfonyl ($\overset{\text{O}}{\underset{\text{O}}{\text{S}}}-\text{Cl}$). The parent structure to which the functional groups were attached varied widely. Ampule storage and glass test cell data showed little improvement in Ca corrosion and/or

TABLE 17 - APROTIC SOLVENT - SOCl_2 COMPATIBILITY

<u>SOLVENT</u>	<u>STABLE</u>	<u>UNSTABLE</u>	<u>OBSERVATIONS</u>
Dimethyl Sulfoxide (DMSO)		X	Violent Gassing
Sulfolane	X		No Reaction
Formamide		X	Exothermic Gassing
N,N - Dimethyl Formamide (DMF)	X		Slight Exothermic
Tetrahydrofuran (THF)	X		No Reaction
N,N - Dimethylacetamide		X	Violent Gassing/ Color Change
N - Methyl Formamide		X	Violent Gassing/ Color Change
Phosphorous Oxychloride	X		No Reaction
Acetonitrile	X		No Reaction
Benzonitrile	X		No Reaction
Dimethyl -3, 3-Thiodipropionate	X		No Reaction

TABLE 18 - APROTICS/SALTS/SOCl₂ COMBINATION COMPATIBILITIES

<u>SALT</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>
AlCl ₃	I	R	I	S	S
Ca-Chloride	I	I	I	I	I
-Iodide	I	I	S	S	I
-Propionate	I	I	I	I	I
-2,4-Pentanedionate	I	R	I	I	I
-Isobutyrate	I	I	I	I	I
-Resinate	I	S	S	I	S
-Benzoate	I	I	S	I	I
-Silicate	I	I	I	I	S
-Lactate	I	I	I	I	I
-Salicylate	S	I	I	I	I
-Salicide	I	I	I	I	I
-Nitrite	I	I	R	I	I
-Alginate	I	I	I	I	I
-Tetrafluoroborate	I	I	I	I	I
-Fumarate	I	I	I	I	I
-Carbonate	I	I	I	I	I
-Bromide	I	I	I	I	I
-Stearate	I	I	I	I	I
-Sulfide	I	I	I	I	I

1 = Dimethyl -3,3 Thiodipropionate

2 - THF

3 = POCl₃

4 = Acetonitrile

5 = Benzonitrile

I = Insoluble

R = Reactive

S = Soluble

TABLE 19 - CaSALTS/SOCl₂
CALCIUM CORROSION STORAGE TEST

+60C

COMPONENTS

Ca Caproate/SOCl ₂	Fail @ 1 wk.
Ca Hypochlorite/SOCl ₂ /Ca (Pol)	Fail @ 8 wk.
Ca Hypochlorite/SOCl ₂ /Ca (Unpol)	Pass @ 16 wk.
CaI ₂ /SOCl ₂	Pass @ 16 wk.
" Laurate/SOCl ₂	Fail @ 1 wk.
" Napthenate/SOCl ₂	Fail @ 1 wk.
" Nitrate/SOCl ₂ (Reaction Products)	Pass @ 16 wk.
" Octoate/SOCl ₂	Fail @ 1 wk.
" 2, 4-Pentanedionate/SOCl ₂	Fail @ 1 wk.
" Propionate/SOCl ₂	Fail @ 1 wk.
SbCl ₄ (Sat)/SOCl ₂	Fail @ 1 wk.
SiCl ₄ /SOCl ₂	Fail @ 1 wk.
WCl ₅ /SOCl ₂ /Ca (Unpol)	Pass @ 16 wk.
(CH ₃) ₄ NCl/SOCl ₂	Pass @ 16 wk.

TABLE 20 - APROTICS/SOCl₂
CALCIUM CORROSION STORAGE TEST

+ 60C

COMPONENTS

POCl ₃	Pass @ 4 wk.
POCl ₃ /SOCl ₂	Pass @ 5 wk.
POCl ₃ /SO ₂ Cl ₂	Pass @ 5 wk.
Benzonitrile	Fail @ 1 wk.
Benzonitrile/SOCl ₂	Pass @ 5 wk.
Benzonitrile/SO ₂ Cl ₂	Pass @ 5 wk.
Acetonitrile/SOCl ₂	Fail @ 1 wk.
Acetonitrile/SO ₂ Cl ₂	Fail @ 1 wk.
Tetrahydrofuran/SOCl ₂	Fail @ 1 day
Tetrahydrofuran/SO ₂ Cl ₂	Fail @ 1 wk.
Dimethyl Formamide (DMF)	Pass @ 5 wk.
DMF/SO ₂ Cl ₂	Fail @ 1 wk.

TABLE 21 - CaSALTS/APROTICS/SOCl₂

CALCIUM CORROSION STORAGE TEST

+ 60C

<u>COMPONENTS</u>	<u>OBSERVATIONS</u>
CaCl ₂ /DMF/10% SOCl ₂	Fail @ 1 wk.
CaCl ₂ /DMF/25% SOCl ₂	Fail @ 1 wk.
CaCl ₂ /DMF/50% SOCl ₂	Fail @ 1 wk.
CaCl ₂ /DMF/10% POCl ₃	Pass @ 6 wk.
CaCl ₂ /DMF/25% POCl ₃	Pass @ 6 wk.
CaCl ₂ /DMF/50% POCl ₃	Pass @ 6 wk.

TABLE 22 - SOCl_2 /INHIBITORS
CALCIUM CORROSION STORAGE TEST

+ 60C

<u>COMPONENTS</u>	<u>OBSERVATIONS</u>
Benzoyl Chloride	Pass @ 5 wk.
Benzoyl Chloride/ SOCl_2	Pass @ 5 wk.
Benzoyl Chloride/ SO_2Cl_2	Pass @ 5 wk.
Acetyl Chloride/ SOCl_2	Pass @ 5 wk.
Acetyl Chloride/ SO_2Cl_2	Fail @ 2 wk.
Propionyl Chloride	Pass @ 5 wk.
Propionyl Chloride/ SOCl_2	Pass @ 5 wk.
Propionyl Chloride/ SO_2Cl_2	Pass @ 5 wk.
Benzene Sulfonyl Chloride	Fail @ 1 day
Benzene Sulfonyl Chloride/ SOCl_2	Pass @ 3 wk.
Benzene Sulfonyl Chloride/ SO_2Cl_2	Pass @ 3 wk.
Dimethyl Sulfamoyl Chloride	Pass @ 3 wk.
Dimethyl Sulfamoyl Chloride/ SOCl_2	Pass @ 3 wk.
Dimethyl Sulfamoyl Chloride/ SO_2Cl_2	Pass @ 3 wk.
Methane Sulfonyl Chloride	Pass @ 5 wk.
Methane Sulfonyl Chloride/ SOCl_2	Pass @ 5 wk.
Methane Sulfonyl Chloride/ SO_2Cl_2	Pass @ 5 wk.

cell performance. See Table 23. Therefore, the more promising solvent/inhibitors were studied in combination with SOCl_2 and AlCl_3 and LiCl . See Table 24. Solvent/Inhibitors which showed the most promise were: Acetyl Chloride, Propionyl Chloride, Benzoyl Chloride. It was determined to study these solvents more closely in glass cells and hermetically sealed S.S. cells (Keepers) having 0.15 in.³ volume.

TABLE 23 - GLASS TEST CELLS @25C

COMPONENT PERFORMANCE SUMMARY

<u>CELL COMPONENTS/SOCl₂</u>	<u>OCV</u>	<u>LOAD</u>	<u>TIME HOURS</u>
1M (CH ₃) ₄ NCl	0.31	-	-
Ca-Octoate	1.15	-	-
CaI ₂	1.71	-	-
0.1M Ca-Propionate	2.20	3300	55
Sat. Ca-Hypochlorite	2.41	3300	3
Sat. Ca-Resinate	1.96	-	-
0.1M 2,4-Pentanedionate	2.40	3300	1.5
Sat. Ca-Benzate	2.03	3300	0
1M Tetrabutyl-NCl ₄	0.50	-	-
Sat. Ca-Isobutyrate	2.05	3300	0
Sat. CaCl ₂ /WCl ₅	1.79	-	-
Sat. CaCl ₂ /SiCl ₄	2.54	3300	0
Sat. CaCl ₂ /SiCl ₄ /10% BCl ₃	1.90	-	-
1M Tetrabutyl-NI/CaCl ₂	0.35	-	-
0.1M 2,4-Pent. 1M Propionate	2.36	3300	-
0.1M 2,4-Pent. 1M Propionate/10% BCl ₃	1.87	-	-
0.1M 2,4-Pent. 10% BCl ₃	1.99	-	-
0.1M Propionate/10% BCl ₃	2.24	3300	55
CaNO ₃	2.71	3300	237
Ca-Perchlorate	3.30	3300	0
Ca-P.Amino Salicylate/Di(CH ₃)Thiodypop./25%	1.15	-	-
" /50%	1.68	-	-
" /75%	0.87	-	-
" /90%	0.52	-	-
1M CaI ₂ POCl ₃ /25%	3.03	3300	200

TABLE 23 - continued

<u>CELL COMPONENTS/SOCl₂</u>	<u>OCV</u>	<u>LOAD</u>	<u>TIME HOURS</u>
IM CaI ₂ POCl ₃ /50%	2.99	3300	216
" /75%	2.89	3300	150
" /90%	2.89	3300	0
0.5M Ca-Resinate/POCl ₃ /25%	2.71	3300	3
" /50%	2.99	3300	3
" /75%	3.10	3300	19
" /90%	2.76	3300	0
Ca-Benzate/POCl ₃ /25%	2.86	3300	0
" /50%	2.86	3300	0
" /75%	3.20	3300	0
" /90%	3.09	3300	0
IM CaI ₂ /POCl ₃ (No SOCl ₂)	2.60	3300	100
0.25M Ca-Resinate/Benzonitrile/90%	2.34	3300	0
0.5M " /THF/90%	1.70	-	-
1.5M AlCl ₃ /Benzoylchloride (no SOCl ₂)	1.98	-	-
" " /25%	3.00	3300	568
" " /50%	3.15	3300	220
" " /75%	3.15	3300	500+
" " /90%	2.98	3300	498
Sat. AlCl ₃ /Acetyl Chloride	2.78	3300	.40
" /Sulfolane(No SOCl ₂)	2.78	3300	.40
1MA1Cl ₃ Benzene Sulfonyl Cl/Sulfolane	2.80	3300	175
2MA1Cl ₃ Dimethyl Sulfonyl/ "	3.10	3300	175+

TABLE 24 - SALT/INHIBITORS/SOCl₂CALCIUM CORROSION STORAGE TEST
+ 60CCOMPONENTS

1.5M AlCl ₃ /Benzoyl Chloride/50% SOCl ₂	Pass @ 4 wk.
1.5M AlCl ₃ /Benzoyl Chloride/25% SOCl ₂	Pass @ 4 wk.
AlCl ₃ /Benzoyl Chloride/SOCl ₂	Pass @ 4 wk.
AlCl ₃ /SO ₂ Cl ₂ /SOCl ₂	Fail @ 30 min.
AlCl ₃ /Methane Sulfonyl Chloride/SOCl ₂	Fail @ 15 hr.
AlCl ₃ /Acetyl Chloride/SOCl ₂	Fail @ 1 wk.
AlCl ₃ /Benzonitrile/SOCl ₂	Fail @ 1 wk.
AlCl ₃ /Acetonitrile/SOCl ₂	Fail @ 15 hr.
AlCl ₃ /Propionyl Chloride/SOCl ₂	Pass @ 5 wk.
1.5M AlCl ₃ /Benzoyl Chloride/75% SOCl ₂	Pass @ 3 wk.
1.5M AlCl ₃ /Benzoyl Chloride/90% SOCl ₂	Pass @ 3 wk.
AlCl ₃ /Dimethyl Sulfonyl Chloride/SOCl ₂	Fail @ 1 wk.
AlCl ₃ /Acetyl Chloride/Sulfolane/SOCl ₂	Fail @ 1 wk.
AlCl ₃ /Benzoyl Chloride/CCl ₄ /SOCl ₂	Fail @ 1 day
AlCl ₃ /Benzoyl Chloride/Sulfolane/SOCl ₂	Fail @ 1 day
AlCl ₃ /Dimethyl Sulfonyl Chloride/Sulfolane/SOCl ₂	Fail @ 1 day
AlCl ₃ /Benzene Sulfonyl Chloride/Sulfolane/SOCl ₂	Fail @ 1 day
AlCl ₃ /Acetonitrile/Sulfolane/SOCl ₂	Fail @ 1 day
AlCl ₃ /Benzonitrile/Sulfolane/AlCl ₃	Fail @ 1 day
Ca Hypochlorite(Sat)/Propionyl Chloride/50% SOCl ₂	Pass @ 1 wk.
CaI ₂ (Sat)/Benzoyl Chloride/50% SOCl ₂	Pass @ 1 wk.
Ca Dichromate(Sat)/Acetyl Chloride/50% SOCl ₂	Pass @ 1 wk.
1.5M AlCl ₃ /Benzoyl Chloride 1%/99% SOCl ₂	Fail @ 2 wk.
" / " 5%/95% SOCl ₂	Pass @ 3 wk.
" / " 10%/90% SOCl ₂	Pass @ 3 wk.
" / " 20%/80% SOCl ₂	Fail @ 1.5 wk.
" / " 30%/70% SOCl ₂	Fail @ 1/2 wk.

Table 24 - continued

COMPONENTS

1.5M continued

AlCl ₃ /Benzoyl Chloride	40%/60%	SOCl ₂	Fail @ 1/2 wk.
" / "	50%/50%	SOCl ₂	Fail @ 1/2 wk.
1.5M LiAlCl ₄ /Benzoyl Chloride	1%/99%	SOCl ₂	Pass @ 3 wk.
" / "	5%/95%	SOCl ₂	Pass @ 3 wk.
" / "	10%/90%	SOCl ₂	Pass @ 3 wk.
" / "	20%/80%	SOCl ₂	Pass @ 3 wk.
" / "	30%/70%	SOCl ₂	Pass @ 3 wk.
" / "	40%/60%	SOCl ₂	Pass @ 3 wk.
" / "	50%/50%	SOCl ₂	Pass @ 3 wk.

SECTION VI

INHIBITOR ACTIVE CELL SERIES

6.1 Hermetically Sealed S.S. Cell Evaluation

Efforts were finally narrowed to Benzoyl Chloride and Propionyl Chloride in the $\text{SOCl}_2/\text{LiAlCl}_4$ system. These two inhibitors have shown the most promise of storability of all inhibitors studied. The mechanism for complexing with AlCl_3 seems to parallel the thionyl chloride/ LiAlCl_4 system.

An electrolyte made by saturating a 1.5M AlCl_3 /Benzoyl chloride solution with LiCl and diluting the mixture with SOCl_2 was used to activate hermetically sealed .15 in³ (Keeper) cells. The electrolyte was diluted into the following benzoyl chloride: thionyl chloride ratios: 20:80, 30:70, 40:60, 50:50, 60:40, and 70:30. Five cells of each concentration were activated. The cathodes measured 0.560" x 0.562" x 1.750" and were made of annealed Calcium which was polished with emery cloth. An exmet 0.005" expanded Ni grid with a 0.002" Ni tab welded on was stamped into the face of the calcium at 10,000 psi. The separator used was Manning glass with 7% polyvinyl acetate binder 0.005" thick. The cathodes were double wrapped in the separator and inserted into the U-shaped anode. The anode tab was spotwelded to the edge of the 304 S.S. can. Therefore, the cells were can negative and terminal positive.

Of the five cells of each concentration, one of each was discharged at room temperature with a 3300-ohm load immediately after activation. The remaining cells were stored at 60C. At one week intervals, one cell of each concentration was removed from storage and discharged with a 3300-ohm load at room temperature, 20C, until all the cells were discharged. The

results are illustrated in Figures 22-27, Table 25. The open circuit voltages (OCV) of the cells in storage were recorded daily and are listed in Table 26.

Ampoules of the electrolytes used were also placed in storage at 60C. The results of the storage test are listed in Table 27.

Internal cell connections between anode Ca and grid were a problem. Spot welds and stamping of the grid into the calcium was ineffective. Corrosion rapidly isolated the grid from the anode.

A glass test cell using 2:1M LiAlCl₄/Acetyl chloride/50% SOCl₂ having one 8% TFE cathode measuring .56" x .68" x .15", with excess calcium anode capacity was constructed and discharged. OCV of the cell was 3.12 volts. The cell ran for 272 hours before reaching 2.0 volts under a 3300-ohm resistive load. Cell discharge data is as follows:

Cathode Volume	0.936 cm ³
Average Potential	2.65
Amp Hours above 2.0 volts	.212
Amp Hours/cm ³ cathode	:226

Further work with acetyl chloride was discontinued, as storage ampoules with this solvent had exploded when in +60°C storage.

TABLE 25 - DISCHARGE DATA S.S. CELLS

LiAlCl₄/Benzoyl Chloride/SOCl₂

Benzoyl Chloride To SOCL ₂	Control		One Week 60C		
	<u>Amp.Hr.</u>	<u>Mat.Utl.</u>	<u>Amp.Hr.</u>	<u>Mat.Utl.</u>	
20/80	0.105	0.13	0.048	0.06	
30/70	0.127	0.16	0.087	0.11	
40/60	0.154	0.19	0.110	0.14	
50/50	0.174	0.22	0.120	0.15	
60/40	0.179	0.22	0.119	0.15	
70/30	0.171	0.21	0.123	0.15	
Two Weeks 60C		Three Weeks 60C		Four Weeks 60C	
<u>Amp.Hr.</u>	<u>Mat.Utl.</u>	<u>Amp.Hr.</u>	<u>Mat.Utl.</u>	<u>Amp.Hr.</u>	<u>Mat.Utl.</u>
0.051	0.06	0.040	0.05	0.003	0.04
0.049	0.06	0.003	0.01	-	-
0.128	0.16	0.071	0.09	-	-
0.120	0.15	0.061	0.08	0.072	0.09
0.124	0.16	0.104	0.18	0.058	0.07
0.117	0.15	0.117	0.15	0.112	0.14

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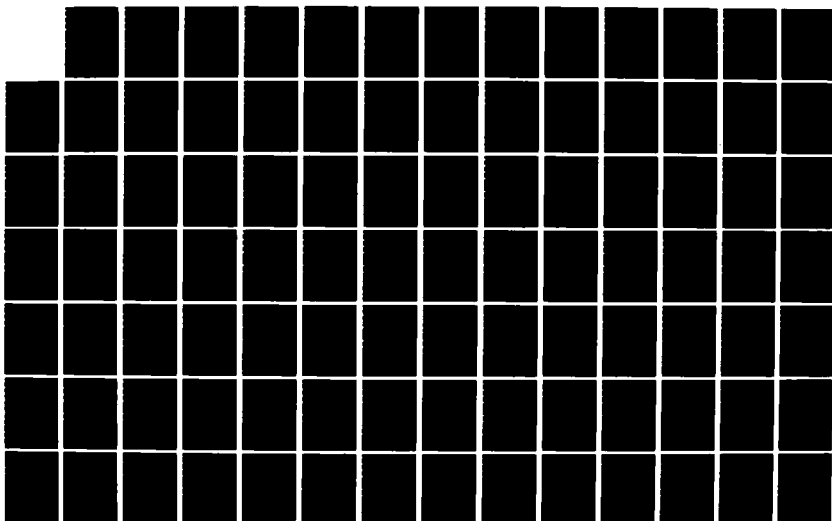
CALCIUM/THIONYL CHLORIDE BATTERY TECHNOLOGY(U)
EAGLE-PICHER INDUSTRIES INC JOPLIN MO ELECTRONICS DIV
T COUNTS DEC 85 AFWAL-TR-85-2081 F33615-81-C-2076

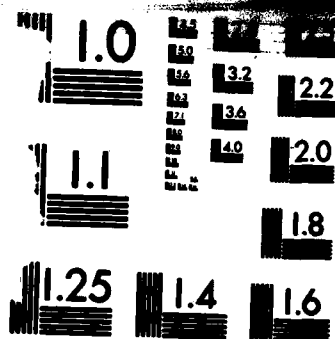
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MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

TABLE 26 - OPEN CIRCUIT VOLTAGES FOR LiAlCl_4 /BENZOYL CHLORIDE/ SOCl_2 IN STORAGE

<u>Cell Number</u>	<u>Days in Storage</u>	<u>OCV (Volts)</u>
20/80 B	7	3.01
	14	3.05
	21	3.05
	28	3.15
30/70 B	7	3.02
	14	3.15
	21	3.12
	28	0.02 (3.18 at 25 days)
40/60 B	7	3.01
	14	3.04
	21	3.04
	28	0.00 (3.05 at 14 days)
50/50 B	7	2.93
	14	3.02
	21	3.08
	28	3.09
60/40 B	7	2.91
	14	3.02
	21	3.07
	28	3.07
70/30 B	7	2.85
	14	2.93
	21	3.03
	28	2.99

TABLE 27 - BENZOYL CHLORIDE INHIBITOR AMPULE EVALUATION AT +60°C

**1.5M LiAlCl₄ in Benzoyl Chloride
diluted with varying amounts of SOCl₂**

Benzoyl Chloride: SOCl₂ (%)	w/LiAlCl₄ at 3 Weeks
1:99	Pass
5:95	Pass
10:90	Pass
20:80	Pass
30:70	Pass
40:60	Pass
50:50	Pass

LIALCL4/BENZ CHL/SOCL2 20/80

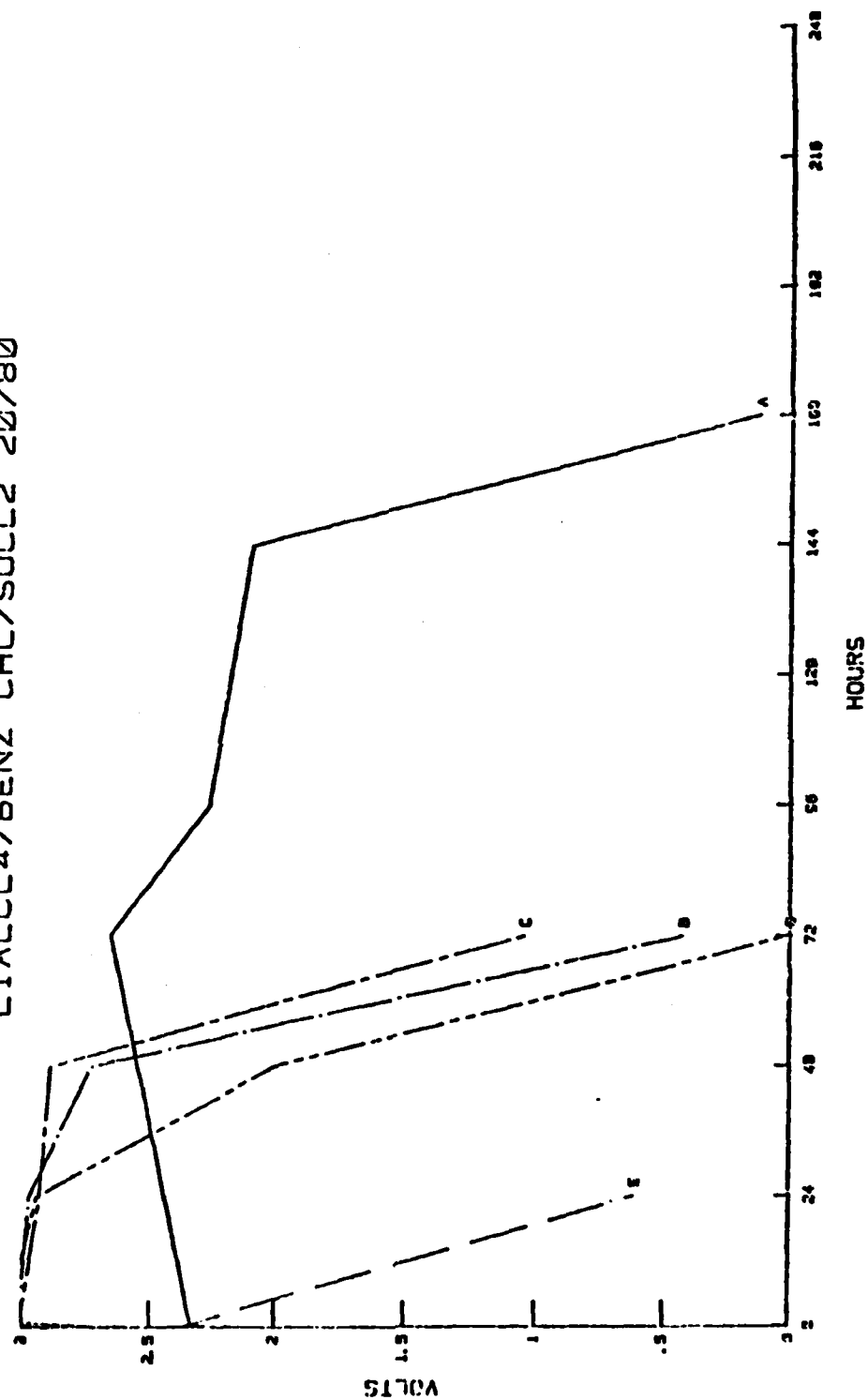


FIGURE 22 Benzoyl Chloride Matrix - 20/80

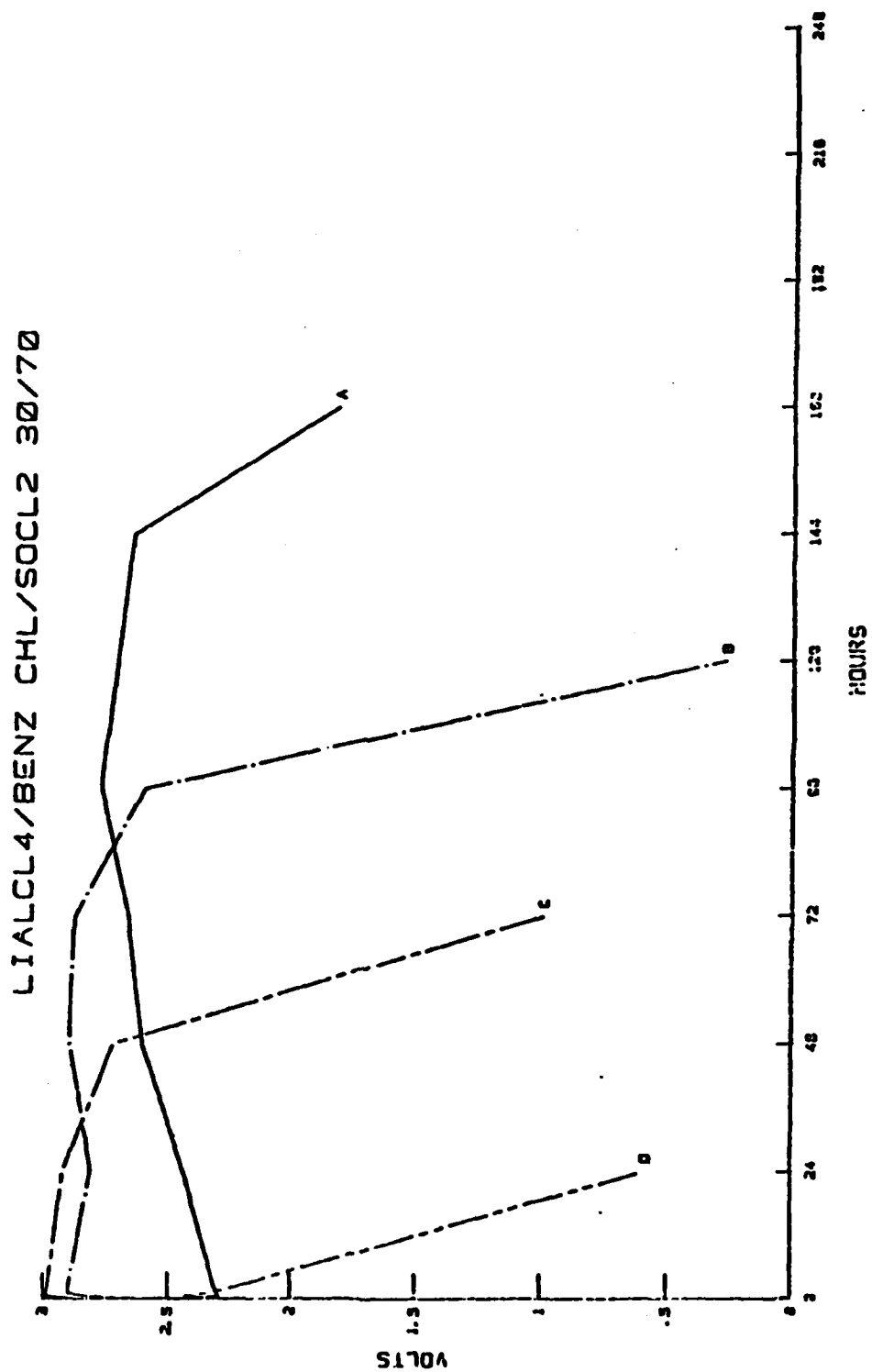


FIGURE 23 Benzoyl Chloride Matrix - 30/70

LIALCL4/BENZ CHL/SOCL2 40/60

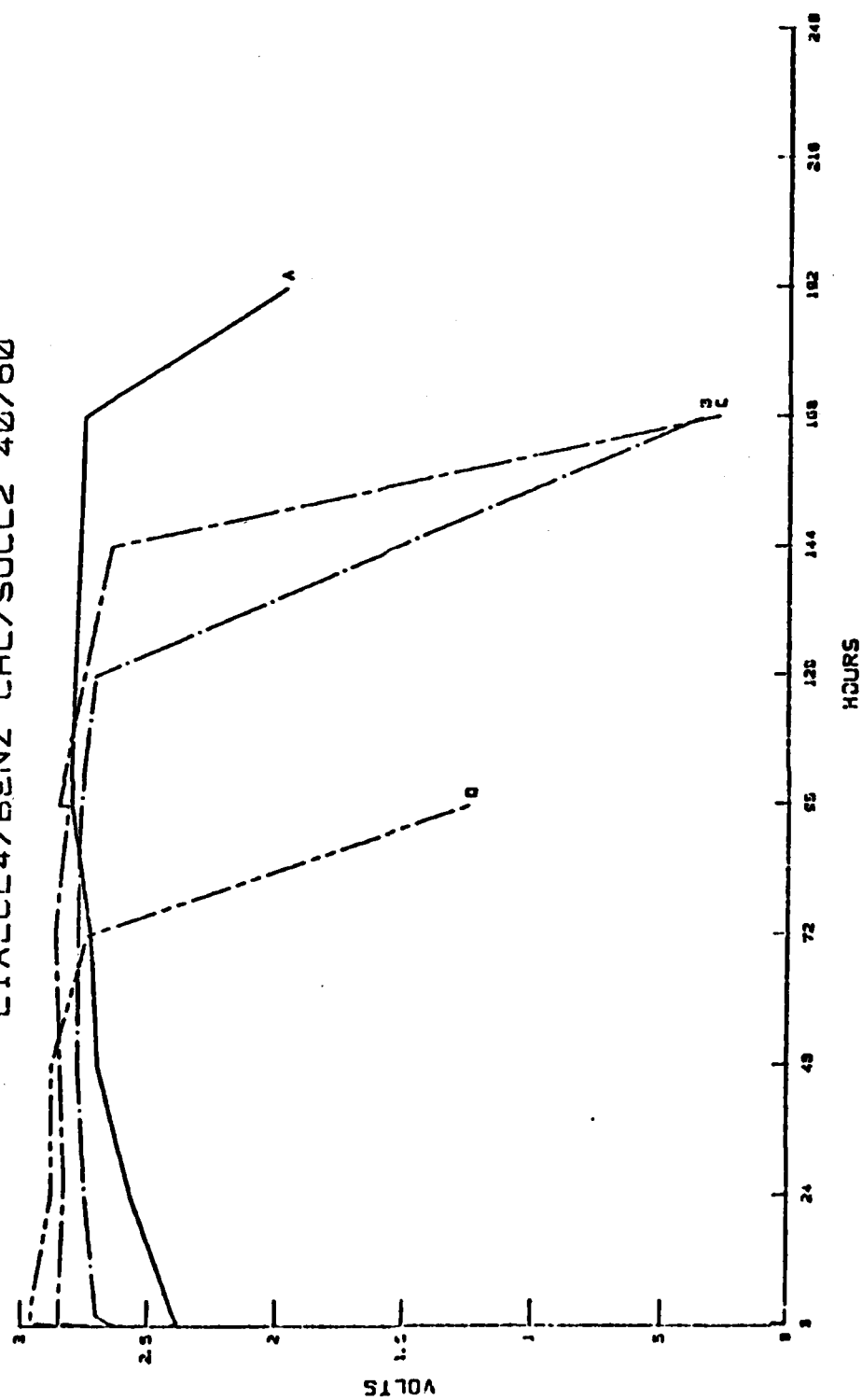


FIGURE 24 Benzoyl Chloride Matrix - 40/60

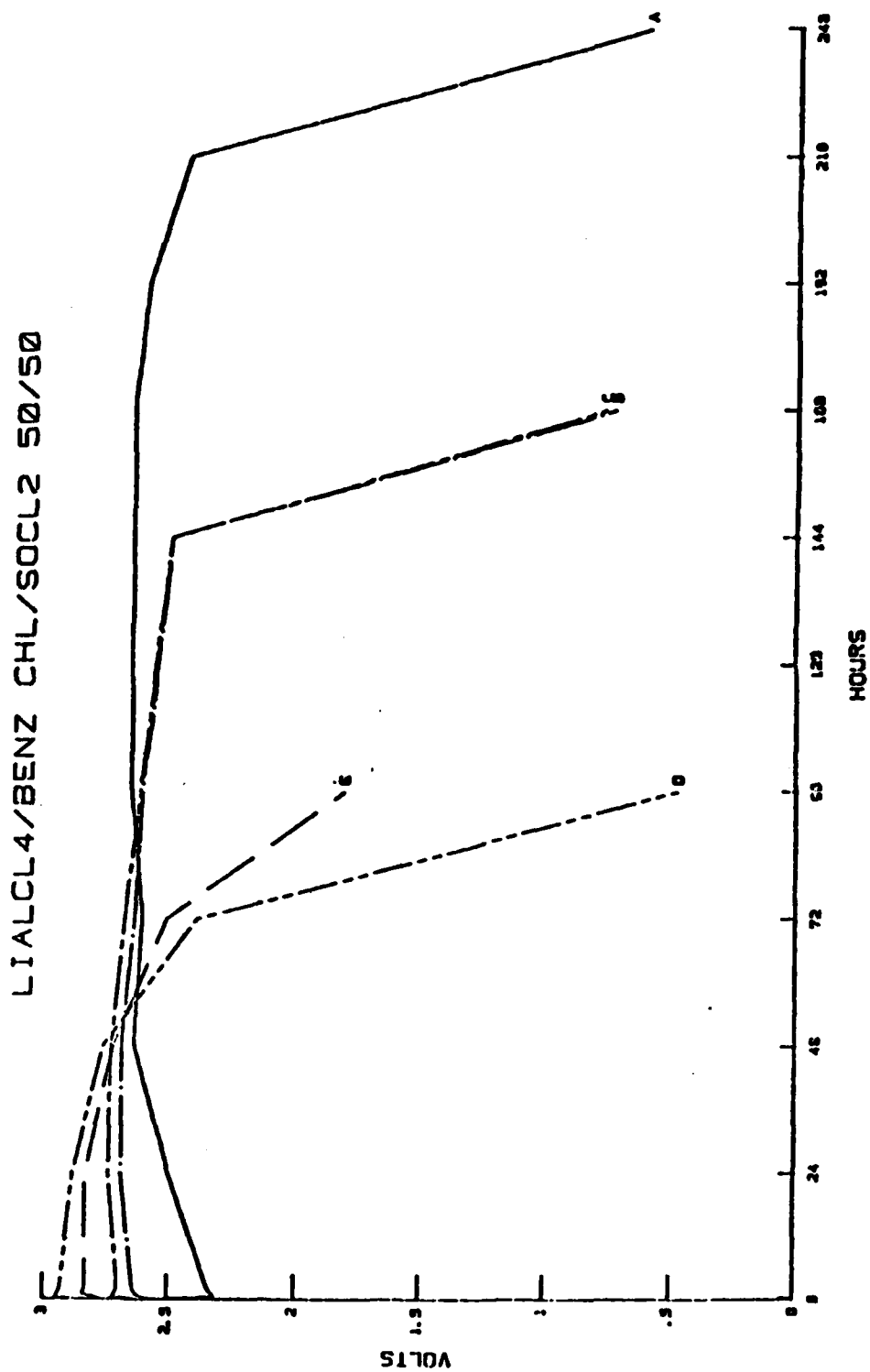


FIGURE 25 - Benzoyl Chloride Matrix - 50/50

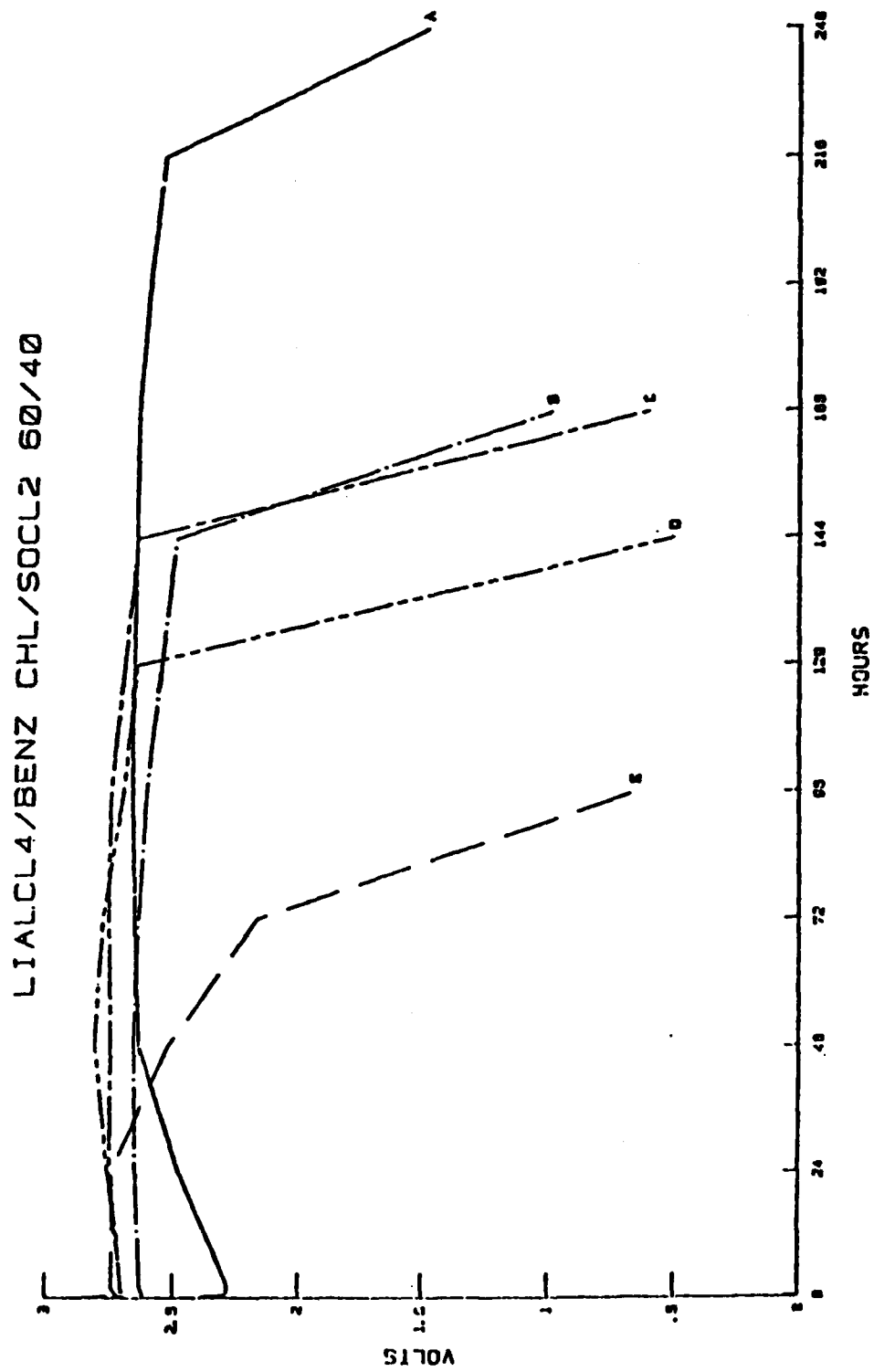


FIGURE 26 Benzoyl Chloride Matrix - 60/40

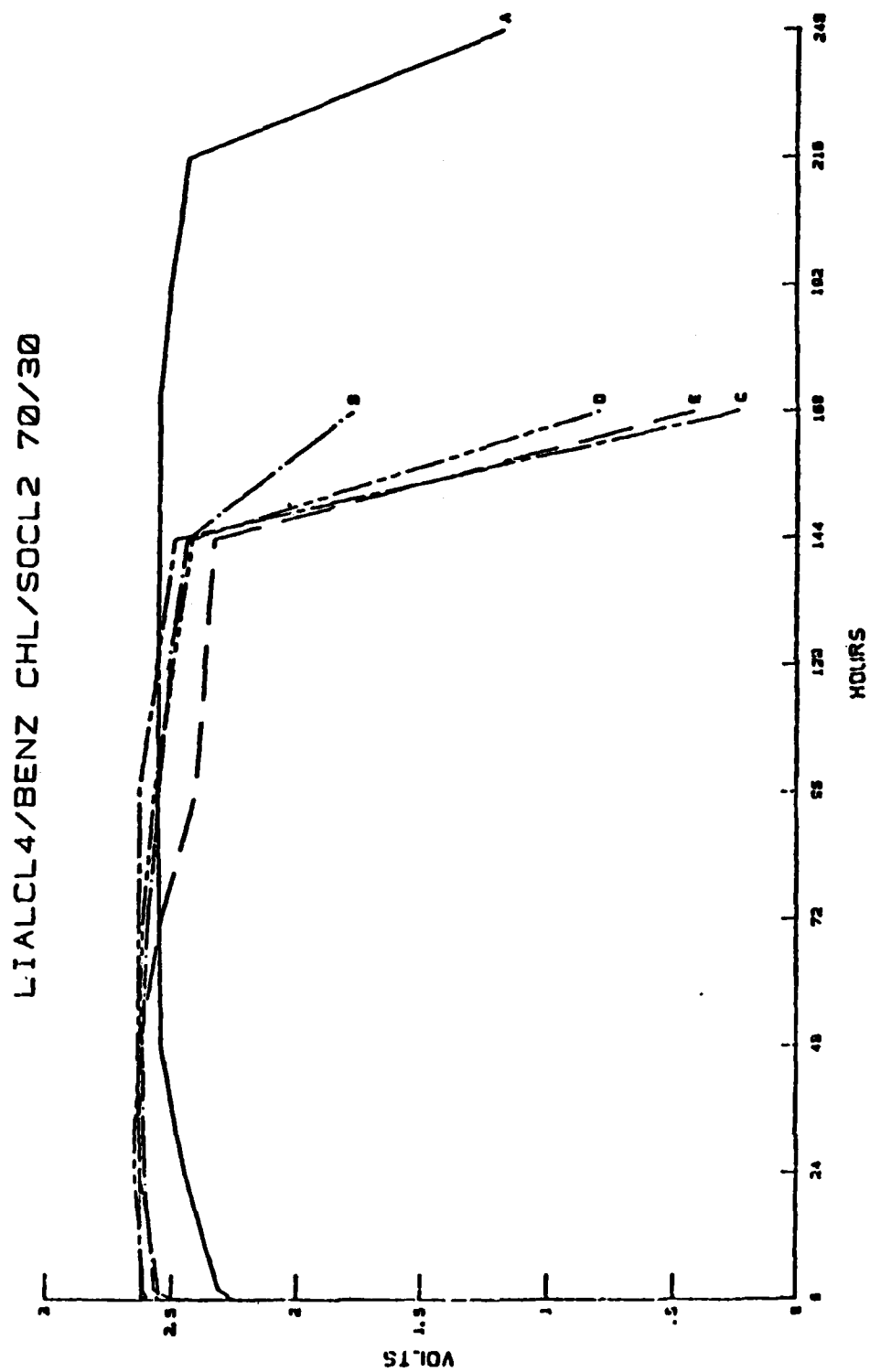


FIGURE 27 Benzoyl Chloride Matrix - 30/30

6.2 Propionyl Chloride - Based Small Cell Work

Thirty hermetically sealed 304 S.S. cells were prepared for heat storage. Each cell measured .650" x .250" x 1.0". Each cathode was dry pressed 10% TFE baked/90% Carbon Black measuring .560" x .700" x .125". The cathode was wrapped by one piece of .020" thick Ca metal (polished) anode large enough to cover the entire cathode. Manning separator was used and all tabs and connections were spot welded. The electrolyte consisted of 3 Molar AlCl_3 /Propionyl Chloride diluted with SOCl_2 in the following concentrations (Propionyl Chloride/ SOCl_2): 20/80, 30/70, 40/60, 50/50, 60/40, 70/30. Five cells were activated at each of the six electrolyte concentrations. One cell from each of the six groups was immediately discharged @ 22C as a control with 3300-ohms load.

All remaining cells were placed in heat storage at +60C. One cell from each concentration level was to be removed from storage and discharged at 1 week intervals. However, all cells in +60C heat storage swelled and vented within the first 24 hours of storage. The highly acidic 3 Molar AlCl_3 may have reacted with the Calcium Anodes causing a pressure build-up due to gas formation. Discharge data for the Control group of cells is as follows:

<u>Electrolyte</u> <u>(Propionyl/SOCl_2)</u>	<u>OCV</u>	<u>Range</u>	<u>Discharge</u> <u>(Hours)</u>	<u>AmpHr</u>	<u>Amp Hr/</u> <u>cm^3</u>
20/80	2.99	2.85-2.88	192*	Incomplete Data	
30/70	3.05	2.93-2.73	192*	"	"
40/60	3.12	3.01-2.14	192*	"	"
50/50	3.13	3.02-2.01	140	0.102	0.127
60/40	3.05	2.95-2.00	135	0.098	0.122
70/30	3.12	3.06-2.02	144	0.107	0.133

*2.0 Volt cut-off occurred during the weekend, all voltages were less than 1.0 the following Monday.

6.3 Calcium Melting Attempt

To alleviate the grid/anode connection problem, a method of forming an anode was tried where the grid was imbedded in the calcium by melting the calcium around the grid. A standard Blue M, firebrick lined, muffle furnace was obtained and altered by fitting it with a gas port so argon could be flushed through the heating chamber. The chamber was purged with argon at room temperature for several minutes. The mold containing the calcium and was placed inside and the chamber was purged for several minutes more. The oven was then turned on and allowed to reach 900°C . It took approximately 45 minutes to reach this temperature. The oven was then turned off and allowed to cool. Argon was flowing continuously through the chamber at all times. The calcium did melt, but impurities in the atmosphere such as O_2 and H_2O caused bubbling and distortion of the metal. Several attempts were made but none succeeded. A controlled atmosphere furnace appears necessary to make this method successful.

6.4 Second Benzoyl Chloride Cell Matrix

A second discharge test for the $1.5\text{M LiAlCl}_4/\text{Benzoyl Chloride}/\text{SOCl}_2$ system was set up. Ampules of the electrolyte concentration being used were also made and placed in storage at 60°C . The results of the ampule tests are listed in Table 28.

The cells being utilized in the second series are of larger volume than those used in the first test, being $0.500'' \times 0.500'' \times 1.875''$. When the header is welded on the total volume inside the cell case is 0.4475 in^3 or 7.3345 cm^3 . This is over 3.5 times as large as the previous cells used. The cathode measures $0.490'' \times 1.650'' \times 0.130''$. The surface area utilized is 0.8085 in^2 or 13.2513 cm^2 . This is only 0.0245 in^2 or 0.4015 cm^2 larger than the surface area of the cathode utilized in the previous cells. This arrangement was chosen to provide an excess of electrolyte which was suspected as a problem in test series 1. The Ca anodes in series 2 measured $0.490'' \times 1.650'' \times 0.045''$

(the Ca initially was 0.050" thick but was polished to 0.045").

The anodes were spot welded to stainless steel spring clips to which a nickel tab was spot welded. The cathodes were placed in the cell case against a bare side. The spring clips and Ca were wrapped in Manning glass separator and inserted into the cell case. The tab was spot welded to the header. The spring provided pressure in the cell case to help insure even contact between the two electrodes, while taking up a small amount of volume. The headers were welded on and the activation port was sealed by forcing a stainless steel ball into the hole. The cells were assembled in a dry room atmosphere.

The electrolyte was prepared from unopened reagents, in a glove box, containing an argon atmosphere. A 1.5M solution of AlCl_3 in Benzoyl chloride was prepared. To this enough LiCl was added to make a 1.5M solution of LiAlCl_4 in Benzoyl chloride. This solution was diluted with SOCl_2 in the following ratios of Benzoyl chloride to SOCl_2 : 50/50, 60/40, 70/30, 80/20. These dilutions were used to activate the cells.

The cells were activated and sealed in the glove box. Five cells of each concentration were activated. One cell of each group of five was discharged with a 3280-ohm load. The remaining four cells of each group were placed in storage at 60°C. At 1 week intervals one cell of each concentration was removed from storage and discharged with a 3280-ohm load, until all the cells had been discharged. The ocv's of the cells in storage were recorded daily. The ocv of various of the cells are shown in Table 29. Discharge results for the cells are given in Table 30. Discharge curves for three cells from each percentage of benzoyl to thionyl are given in Figures 28 to 31.

The main problems in the first series seemed to be lack of sufficient electrolyte and bad connections between the Ca and the nickel grid. The electrolyte problem was alleviated by using a larger volume cell while maintaining roughly the same sized electrodes. The second problem was addressed by the use of the spring clips in the second series of cells. It was hoped that even if the welded connection failed, the spring action of the clip would be sufficient to maintain electrical contact for discharge.

TABLE 28 - Ca AMPULE STORAGE TEST RESULTS

Ampule Contents	3 Weeks
	Pass/Fail
1. 50/50 1.5 <u>M</u> LiAlCl ₄ /Benzoyl Chl/SOCl ₂	Pass
2. 60/40 1.5 <u>M</u> LiAlCl ₄ /Benzoyl Chl./SOCl ₂	Pass
3. 70/30 1.5 <u>M</u> LiAlCl ₄ /Benzoyl Chl./SOCl ₂	Pass
4. 80/20 1.5M LiAlCl ₄ /Benzoyl Chl./SOCl ₂	Pass
5. Benzoyl Chloride	Pass
6. SOCl ₂	Pass
7. 50/50 Benzoyl Chloride/SOCl ₂	Pass

TABLE 29 - OCV'S OF CELLS IN STORAGE

<u>CELL NO.</u>	<u>OCV</u>	<u>HOURS IN STORAGE</u>
50/50 C	2.93	264 Hrs.
50/50 D	2.93	264 Hrs.
50/50 E	2.92	264 Hrs.
60/40 C	2.89	264 Hrs.
60/40 D	2.90	264 Hrs.
60/40 E	2.87	264 Hrs.
70/30 B	2.77	144 Hrs. (0.003 @ 168 Hrs.
70/30 D	2.79	168 Hrs. (0.002 @ 192 Hrs.
70/30 E	2.83	264 Hrs.
80/20 D	2.84	264 Hrs.
80/20 E	2.82	264 Hrs.

TABLE 30 - SECOND SERIES BENZOYL CHLORIDE CELL RESULTS

<u>Cell No.</u>	<u>Average Potential</u>	<u>Volt Hours</u>	<u>Amp Hours</u>	<u>Watt Hours</u>	<u>Matrix Utilization</u>	<u>Energy Density</u>
50/50 A	2.56	1924.26	0.58	1.48	5.52 AH/in ³	3.32 Watt Hr/in ³
50/50 B	2.54	2101.14	0.64	1.63	6.10	3.63
50/50 C	Failed in storage					
50/50 D	Failed in storage					
50/50 E	2.59	1866.12	0.57	1.48	5.43	3.30
60/40 A	2.34	899.28	0.27	0.63	2.57	1.41
60/40 B	2.56	1840.20	0.56	1.43	5.33	3.20
60/40 C	2.62	1540.62	0.47	1.23	4.48	2.75
60/40 D	Failed after 2 Hr.					
60/40 E	Failed in storage					
70/30 A	2.39	2122.56	0.64	1.53	6.10	3.42
70/30 B	Failed in storage					
70/30 C	2.48	1817.40	0.55	1.36	5.24	3.05
70/30 D	Failed in storage					
70/30 E	2.54	1830.24	0.55	1.40	5.24	3.12

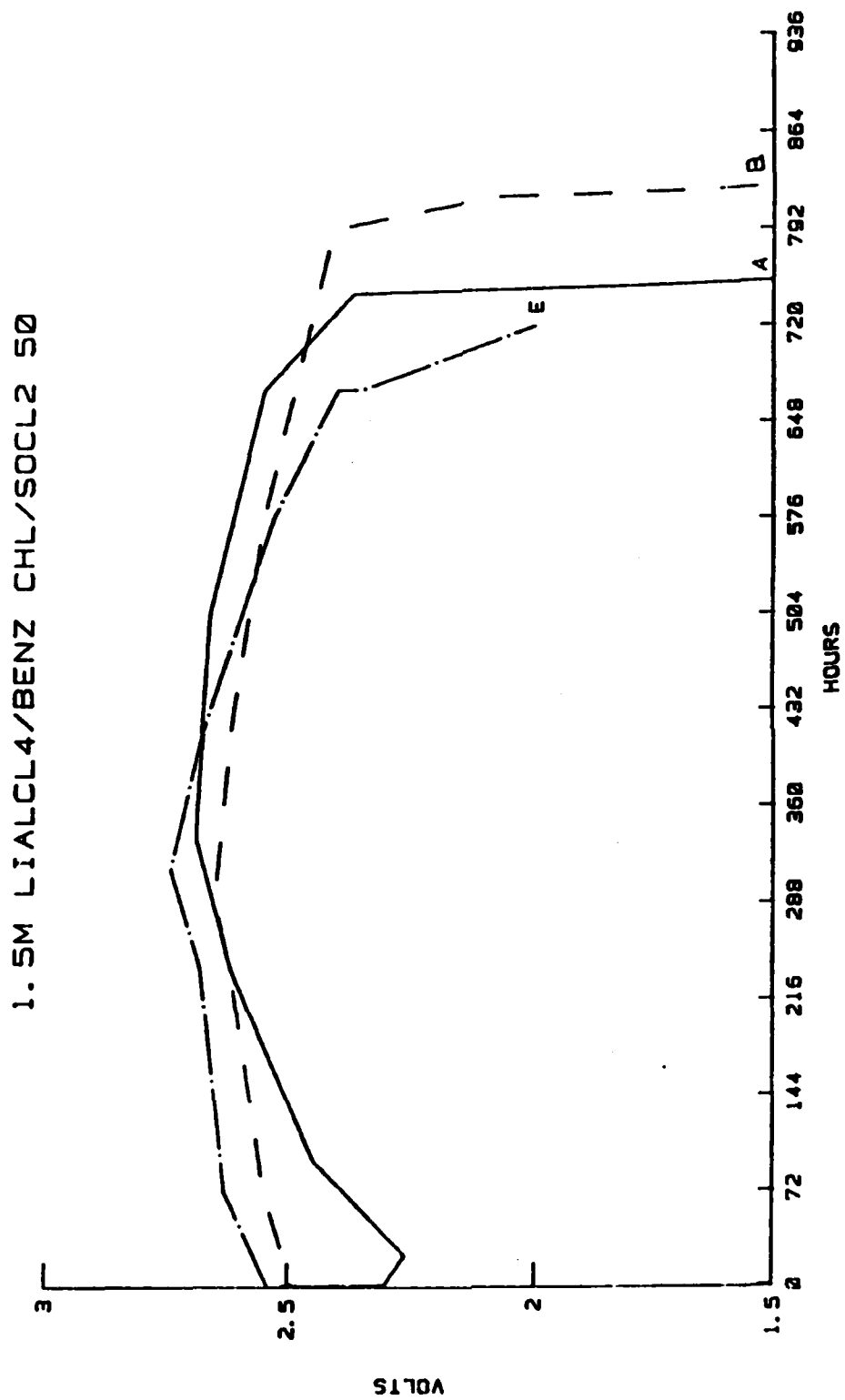


FIGURE 28 Benzoyl Chloride Storage Matrix - 50/50

1.5M LiAlCl₄/BENZ CHL/SOCL₂ 60

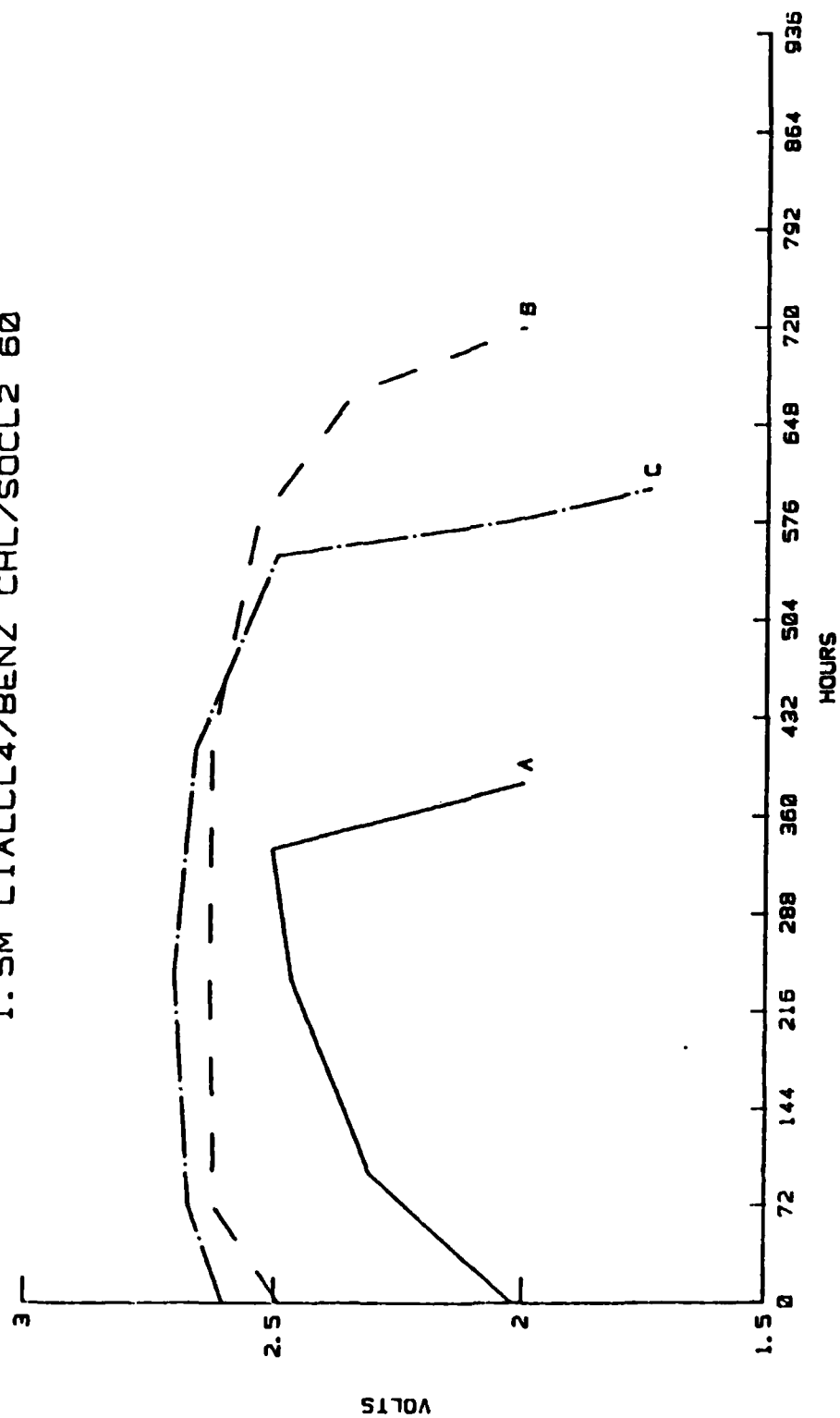


FIGURE 29 Benzoyl Chloride Storage Matrix - 40/60

1.5M LiAlCl₄/BENZ CHL/SOCL₂ 70

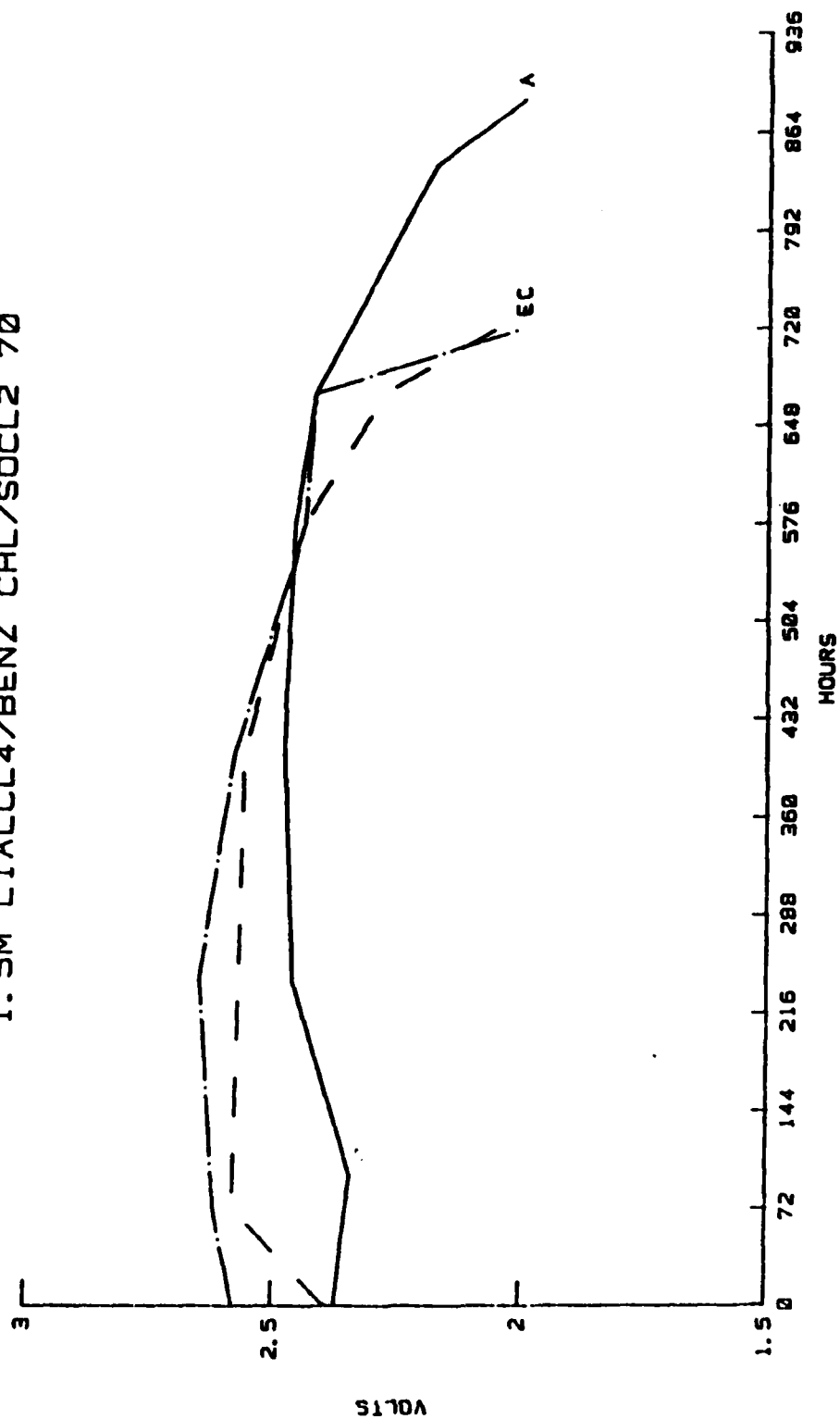


FIGURE 30 Benzoyl Chloride Storage Matrix - 30/70

1.5M LiAlCl₄/BENZ CHL/SOCL₂ 80

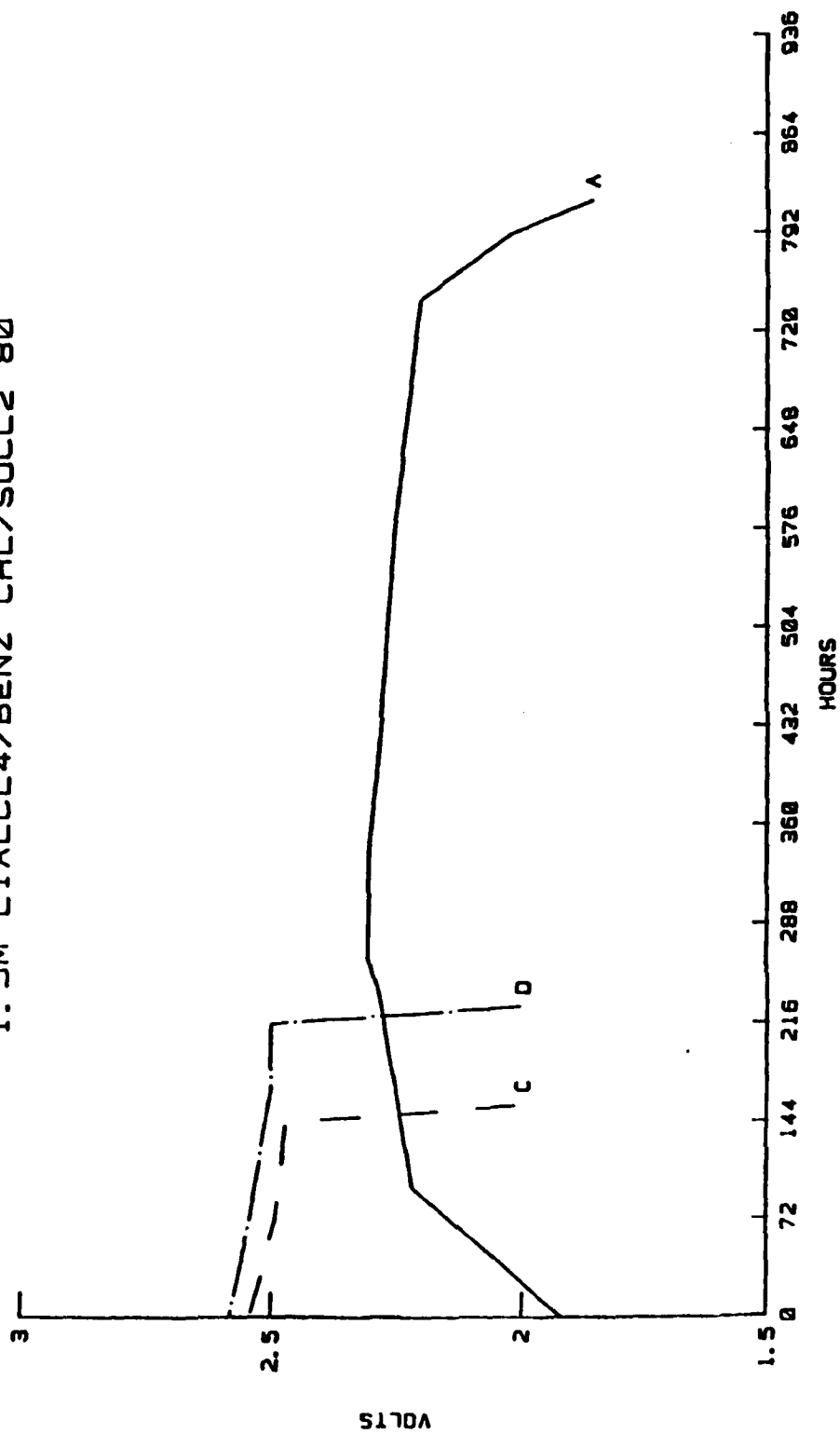


FIGURE 31 Benzoyl Chloride Storage Matrix - 20/80

Based on the discharge curves and length of discharge, the 50:50 benzoyl to thionyl electrolyte mix cells performed the best, closely followed by the cells with a 70:30 mix. Performance for the cells that maintained anode/collector contact were better than that obtained in the first series of test cells, approaching the performance results of the glass test cells.

6.5 Benzoyl/Thionyl Dissection Results

Dissection of the completed test cells showed that those with extended discharge time were still wet with excess electrolyte, had brittle, hard cathodes and putty-like calcium residue. Fresh cells were constructed using a used cathode with a new anode and fresh electrolyte. Most showed good ocv but none would hold load under even the 3300 ohm resistor, indicating the cells were cathode limited. All cells that failed prematurely were found to have no connection between the spring clip and the calcium.

The ampules constructed at the time of cell construction all showed similar appearances. The film of CaCl_2 on the calcium surface appears to be only semi-stable. Some flaking of the layer did occur, however, there was no evidence of uneven corrosion or pitting on the calcium surface. There appeared to be no diminution in the thickness of the Ca.

6.6 Vapor-Deposited Calcium Anodes

The effectiveness of vapor deposited calcium metal on nickel foil (bimetal) was investigated in two test batteries. The bimetal was formed by vapor depositing 0.020" Ca metal on one side of 0.005" Ni foil. It was hoped the bimetal would improve the connection problems now experienced with

with spot welding Ni tabs directly to the calcium. Each battery contained two cells, 3 cathodes/cell. Cells were connected in series. The batteries were discharged at the disappointing rate of 7.5 mA/cm² and 4.5 mA/cm², respectively, with 2:1 electrolyte. Normal discharge should be 20 mA/cm². The batteries were discharged using a constant resistive load. Discharge voltage started dropping immediately and continued dropping throughout the discharge. Autopsy of the two batteries showed approximately 80-90% of the Ca anode surface area covered with a thin dense hard black film which was difficult to scrape from the calcium. A fresh piece of Ca bimetal was soaked in fresh 2:1 electrolyte for 10-15 minutes. The black film appeared randomly over the surface of the calcium, however, not to the same extent as the Ca anodes of the batteries.

SECTION VII

50/50 BENZOYL CHLORIDE/SOCl₂ CELL MATRIX

7.1 Matrix Construction

A matrix of 30 cells, constructed identically to the previous set used to evaluate thionyl/SOCl₂ percentages, was activated with 1.5M LiAlCl₄ 50/50 Benzoyl Chloride, and placed in room temperature storage. Groups of five cells were discharged at 1 month intervals. The first group of five cells was placed on discharge the day after activation. Discharge results are given in Table 31. Discharge curves for the first five cells and the remainder of the storage cells of this matrix are given in Appendix B of this report.

TABLE 31 - 50/50 BENZOYL/SOCl₂ CELL DISCHARGE DATA SET #1

	<u>RT1</u>	<u>RT2</u>	<u>RT3</u>	<u>RT4</u>	<u>RT5</u>
Discharge Temp.	-	-	Room Temperature	-	-
Length of Time on OCV	0	0	0	0	0
OCV	2.64	2.68	2.69	2.68	2.68
Load (OHM)	3300	3300	3300	3300	3300
Discharge Time(Hours)	552	552	696	720	360
Discharge Time (Days)	24	24	29	30	15
\bar{V}	2.61	2.58	2.60	2.53	2.55
V Hr	1445	1426	1808	1825	917
A Hr	0.44	0.43	0.55	0.55	0.28
Watt Hr	1.15	1.11	1.43	1.39	0.71
A Hr/cm ³	0.25	0.25	0.32	0.32	0.16

Autopsy of the discharged cells revealed at least 50% of the electrolyte remained. The Calcium anode in each cell was thick paste. All cathodes were semibrittle with minimal swelling.

Daily discharge data shows no indication when a cell is about to die. Discharge voltage is consistent and then suddenly drops to zero by the following day.

7.2 One Month Storage Results

The second set of 5 cells containing 1.5M LiAlCl₄ 50/50 benzoyl chloride was placed on discharge after 1 month of storage at room temperature (22°C). Discharge results are given in Table 32. Discharge curves for the cells are given in Appendix B of this report.

TABLE 32 - 50/50 BENZOYL/SOCl₂ CELL DISCHARGE DATA SET #2

	<u>RT6</u>	<u>RT7</u>	<u>RT8</u>	<u>RT9</u>	<u>RT10</u>
Discharge Temp.	22C	22C	22C	22C	22C
Length of Time on OCV (Days)	31	31	31	31	31
OCV	2.82	2.78	2.84	2.86	2.83
Load (Ohm)	1650	3300	3300	3300	1650
Discharge Time (Hours)	240	264	552	552	264
Discharge Time (Days)	10	11	23	23	11
\bar{V}	2.62	2.64	2.56	2.60	2.55
V Hr	628	698	1415	1438	672
A Hr	0.38	0.21	0.43	0.43	0.41
Watt Hr	1.00	0.56	1.10	1.13	1.04
A Hr/cm ³	0.21	0.12	0.24	0.24	0.23

Autopsy of the discharged cells revealed that at least 50% of the electrolyte remained. The cathodes broke apart upon removal from the cell case but appeared to be semibrittle. The calcium anodes in cells RT6 and RT10 were rigid, partially deteriorated, with mushy surfaces. The calcium anodes in the remaining cells numbered RT7, RT8 and RT9 were mushy with absolutely no structural integrity. Weight of the remaining anode material in cells RT8 and RT9 was 1.4g and 1.6g, respectively. As mentioned for the first set of cells, daily discharge data shows no indication when a cell is about to die. Discharge voltage is consistent and then quickly drops to zero by the following day.

7.3 Two Month Storage Results

The third set of 5 cells containing 1.5M LiAlCl₄ 50/50 benzoyl chloride was placed on discharge after 2 months of storage at room temperature (20°C). Discharge results are given in Table 33. Discharge curves for the cells are given in Appendix B of this report.

TABLE 33 - 50/50 BENZOYL/SOCl₂ CELL DISCHARGE DATA SET #3

	<u>RT11</u>	<u>RT12</u>	<u>RT13</u>	<u>RT14</u>	<u>RT15</u>
Discharge Temp.	22C	22C	22C	22C	22C
Length of Time on OCV (Days)	58	58	58	58	58
OCV	2.94	2.77	2.81	2.84	2.82
Load (Ohm)	1650	3300	3300	3300	1650
Discharge Time (Hours)	360	576	576	576	312
Discharge Time (Days)	15	24	24	24	13
\bar{V}	2.37	2.56	2.60	2.52	2.46
V Hr	853	1477	1501	1453	767
A Hr	0.52	0.45	0.45	0.44	0.46
Watt Hr	1.23	1.15	1.17	1.11	1.13
Allr/cm ³	0.29	0.25	0.25	0.25	0.26

Autopsy of the discharged cells showed nothing unusual. Findings were consistent with previous results.

Cell RT18 was randomly chosen from the fourth set of cells and autopsied prior to the remaining 4 cells of the set being discharged. This was done to study the effects of 3 months OCV. The RT18 calcium showed no signs of corrosion, discoloration or deterioration. The spot welds were intact. The cathode was crumbly but intact.

7.4 Three Month Storage Results

The fourth set of 5 cells containing 1.5M LiAlCl₄ 50/50 benzoyl chloride was placed on discharge after 3 months of storage at room temperature. Discharge results for RT16, RT17, RT19 and RT20 are given in Table 34. Discharge curves for the cells are included in Appendix B to this report.

TABLE 34 - 50/50 BENZOYL/SOCl₂ - CELL DISCHARGE DATA SET #4

	<u>RT16</u>	<u>RT17</u>	<u>RT18</u>	<u>RT19</u>	<u>RT20</u>
Discharge Temp.	22C	22C	22C	22C	22C
Length of Time on OCV (Days)	88	88	88	88	88
OCV	2.83	2.83	A	2.83	2.86
Load (Ohm)	1650	3300	U	3300	1650
Discharge Time (Hrs.)	432	456	T	576	144
Discharge Time (Days)	18	19	0	24	6
\bar{V}	2.64	2.65	P	2.59	2.54
V Hr	1141	1210	S	1493	365
A Hr	0.69	0.37	1	0.45	0.22
Watt Hr	1.82	0.98	E	1.16	0.56
A Hr/Cm ³	0.39	0.21	D	0.25	0.12

The remaining cells, RT16-RT20 were autopsied after discharge. The calcium anodes were mushy, crystalline, and gray in color. The cathodes were crumbly in texture and the surface next to the anode was brittle. Approximately 50% of the electrolyte remained. All spot welds were intact.

7.5 Four Month Storage Results

The fifth set of five cells containing 1.5M LiAlCl₄ 50/50 benzoyl chloride was placed on discharge after 4 months of room temperature storage. Discharge results are given in Table 35. Discharge curves for the cells are given in Appendix B of this report.

TABLE 35 - 50/50 BENZOYL/SOCl₂ - CELL DISCHARGE DATA, SET #5

	<u>RT21</u>	<u>RT22</u>	<u>RT23</u>	<u>RT24</u>	<u>RT25</u>
Discharge Temp.	22C	22C	22C	22C	22C
Length of Time on OCV (Days)	120	120	120	120	120
OCV	2.83	2.86	2.82	2.85	2.85
Load (Ohm)	1650	3300	3300	3300	1650
Discharge Time (Hours)	168	432	504	576	264
Discharge Time (Days)	7	18	21	24	11
\bar{V}	2.55	2.65	2.58	2.58	2.49
V Hr	429	1145	1301	1488	657
A Hr	0.26	0.35	0.39	0.45	0.40
Watt Hr	0.66	0.93	1.01	1.16	1.00
A-Hr/cm ³	0.15	0.20	0.22	0.25	0.23

Cells RT21-RT25 were autopsied after discharge. The Calcium anodes were mushy, crystalline, and gray in color. The cathodes were crumbly in texture and the surface next to the anode was brittle. Approximately 50% of the electrolyte remained. All spot welds were intact.

7.6 Five Month Storage Results

The sixth and final set of cells containing 1.5M LiAlCl₄ 50/50 benzoyl chloride was placed on discharge after 5 months of room temperature storage. Discharge results are given in Table 36. Discharge curves for the cells are given in Appendix B to this report.

TABLE 36 - 50/50 BENZOYL/SOCl₂ - CELL DISCHARGE DATA, SET #6

	<u>RT26</u>	<u>RT27</u>	<u>RT28</u>	<u>RT29</u>	<u>RT30</u>
Discharge Temp.	22C	22C	22C	22C	22C
Length of Time on OCV (Days)	150	150	150	150	150
OCV	2.88	2.84	2.84	2.91	2.84
Load (Ohm)	1650	3300	1650	3300	1650
Discharge Time (Hours)	312	624	552	456	216
Discharge Time (Days)	13	26	23	19	9
\bar{V}	2.47	2.62	2.60	2.61	2.56
V Hr	712	1635	1436	1192	553
A Hr	0.43	0.49	0.44	0.36	0.34
Watt Hr	1.06	1.28	1.14	0.94	0.87
A Hr/Cm ³	0.243	0.280	0.246	0.204	0.189

Cells RT26-RT30 were autopsied after discharge. The calcium anodes were mushy, crystalline, and gray in color. The cathodes were crumbly in texture and the surface next to the anode was brittle. Approximately 50% of the electrolyte remained. All spot welds were intact.

Overall results from this test matrix were encouraging. While a fair A-Hr variability was exhibited from cell to cell, storability was quite reasonable. However, the discharge rate for these cells was quite low, being on the order of either 1 or 2 ma.

SECTION VIII

THIRD PHASE ACTIVE CELL ELECTROLYTE INVESTIGATION

8.1 LiAlCl₄ Storage Matrix

An ampoule storage test was constructed to verify the earlier results obtained with LiAlCl₄ based electrolytes. Pfizer .010" Ca, 99.9% pure, both polished and unpolished, as well as .050" thick 99% pure Pfizer calcium was placed in ampoules along with test electrolyte, then flame sealed. Ampoules were constructed in a glove box, then removed to room air for sealing due to argon atmosphere in the glove box. Ampoule results are given in Table 37.

As can be seen from Table 37, all ampoules eventually developed severe Ca corrosion. As expected the ampoules containing unbalanced (higher molar content of AlCl₃ than LiCl) electrolyte corroded quite quickly. The altered Lithcoa electrolytes, whether increased in salt concentration or diluted, corroded more quickly than the unaltered electrolyte. As expected, the unpolished (as received) calcium, which has a light tarnish layer, resisted corrosion longer than the corresponding calcium which had been polished using a stainless steel bristle brush.

8.2 LiCl Replacement Work

Instead of LiCl with AlCl₃, NaCl and KCl were tried as replacement salts, to yield NaAlCl₄ and KAlCl₄, respectively. KCl proved to be too insoluble in thionyl chloride to be of any practical value. NaCl dissolved readily in thionyl chloride, and was tested further. Glass cell tests, using 2:1 AlCl₃ to NaCl molar ratio electrolyte, were tried. However, at a practical reserve cell rate 25-ohm load, the voltage of the cells never rose above 2.0 volts. Glass test cells utilizing 1.5M NaAlCl₄ electrolyte were tried at a practical active cell load, 350 ohms. Results, while not spectacular,

TABLE 37 - Ca/SOCl₂ - AMPULE STORAGE

	1.5M LiAlCl ₄ Lithcoa						
	0.75M LiAlCl ₄		2:2 Enhanced		As Received		Pol. .050"
	Pol.	Unpol.	Pol.	Unpol.	Pol.	Unpol.	
	.010	.010	.010	.010	.010	.010	
First 24 Hours (Room Temp.)	NC	NC	NC	NC	NC	NC	NC
+60°C							
First Signs of Corrosion (Hours)	48	48	48	120	48	720	120
Severe Corrosion (Hours)	120	720	168	168	720	1680	1152
	Lab Prepared Electrolyte						
	2:2		Discharged		2:1		
	Pol.	Unpol.	Pol.	Pol.	Unpol.	Pol.	
	.010	.010	2:1			.050	
First 24 Hours (Room Temp.)	NC	NC	Dis- Colored	-	-	-	
+60°C							
First Signs of Corrosion (Hours)	48	120	24	1	1	3	
Severe Corrosion (Hours)	168	240	48	3	3		

were reasonable, with a .3 AH/cm³ matrix utilization and \bar{V} of 2.53. However, storage ampoules made up utilizing the electrolyte and Ca foil, stored at +60°C, showed visible corrosion within 24 hours, and serious corrosion within 4 days, so no further testing was undertaken.

8.3 Cr +6 SALT WORK

Potassium chromate (K_2CrO_4) and potassium dichromate ($K_2Cr_2O_7$) were tried as electrolyte salts in thionyl chloride. The reagent grade salts were vacuum dried for 16 hours at 160°C. Solubility of the salts in thionyl chloride at the 0.5M level was then checked. Neither salt would dissolve completely at this level, with the potassium dichromate showing signs of reaction. This was likely due to the drying regime being unable to convert the dihydrate dichromate past the monohydrate stage. The electrolytes as prepared were tried in glass test cells but both failed to produce ocv's above 2.0. Storage ampoules of the electrolytes w/Ca stored for 10 days. at +60°C with no visible signs of corrosion developing.

8.4 Carbon/Binder Matrix

A matrix was set up to evaluate two different carbons and percent of binder used against the Shawinigan 50% compressed carbon that had been utilized to date. Ketjenblack, from Noury Co., and Blackpearls 2000, from Cabot Corp. were the comparison carbons. It was hoped that more highly structured carbons with increased surface areas compared to the Shawinigan carbon would prove to be more resistant to discharge product plugging and consequent deactivation.

The standard cathode fabrication technique, to this point, had been to press the dry mix onto grid, then bake (sinter) the resulting cathodes to flow the teflon and bind the carbon. It had been shown in earlier work that comparatively high binder levels hindered cathode performance but had been necessary for mechanical handling stability when this cathode fabrication method was employed. An alternate technique was employed with the cathodes tested in this matrix, to determine if equivalent or improved performance could be achieved at the same or lower binder level. In this alternate cathode fabrication technique, the dry cathode mix is suspended in water, then filtered. Two portions of the wet layer thus produced are "sandwiched" with grid, then pressed at first 100, then 2500 psi between blotter paper. The cathodes are then jigged between aluminum plates to air dry for 16 hours, then sintered at 550°F for 20 minutes. A final drying is done at 160°F for a minimum 72 hours. While more complicated, this method had been found to produce plates of excellent handling qualities at comparatively low binder levels. This method is referred to in the data table as "Pasted/Baked".

The results of the carbon/binder testing are given in Table 38. Glass cells were employed for the testing, using the stated cathode, Manning separator,

TABLE 38 - CARBON/BINDER TEST MATRIX

<u>TRIAL</u>	<u>CATHODE TYPE</u>	<u>CATHODE SIZE (Inches)</u>	<u>LOAD (OHMS)</u>	<u>ELECTRO- LYTE</u>	<u>OCV</u>	<u>DISCHARGE TIME (HOURS)</u>	<u>\bar{V}</u>	<u>AHR</u>	<u>AHR/ AHR</u>
I	1 Shawinigan 15%	.710x.525 x .040	350	Benzoyl Cl 50/50	2.42	1½	2.05	0.01	0.030
	2 Pasted/ Baked	.685x.540 x .040	350	SOCl ₂	2.44	1½	2.05	0.01	0.030
II	1 Shawinigan 15% TFE	.710x.535 x .042	350	1.5M LiAlCl ₄ + excess	2.80	16½ Hrs.	2.63	0.124	0.475
	2 Pasted/ Baked	.705x.545 x .040	350	LiCl	2.88	15½ Hrs.	2.62	0.116	0.46
III	1 Shawinigan	.685x.520 x .035	350	1.5M LiAlCl ₄	2.81	13	2.49	0.09	0.453
	2 Pasted/ Baked	.690x.530 x .040	350	SOCl ₂ +LiCl	2.84	13	2.57	0.10	0.397
IV	1 Acetoned Shawinigan 15% TFE	.690x.540 .042	350	1.5M LiAlCl ₄ + excess	2.81	15 Hrs.	2.64	0.113	0.442
	2 Pasted/ Baked	.700x.540 x .040	350	LiCl	2.81	15 Hrs.	2.60	0.111	0.449
V	1 Ketjenblack 7.5% TFE	.705x.550 x .040	350	1.5M LiAlCl ₄ + excess	2.79	12½ Hrs.	2.71	0.097	0.381
	2 Pasted/ Baked	.700x.545 x .040	350	LiCl + excess	2.79	14½ Hrs.	2.67	0.111	0.442
VI	1 Black Pearls 7.5% TFE	.685x.550 x .040	350	1.5M LiAlCl ₄	2.77	10½ Hrs.	2.67	0.078	0.317
	2 Pasted/ Baked	.665x.545 x .040	350	LiCl	2.80	12½ Hrs.	2.67	0.095	0.401

and .010" thick calcium anodes. Utilizing the Ahr/cm^3 data for comparison purposes, it can be seen that while no vast differences were found in any of the carbon/binder combinations tested, the Shawinigan carbon with 15% TFE binder performed best.

The load chosen, 350 ohms, was utilized as producing a ma/cm^2 rate in the 1-1.5 ma/cm^2 range, which was considered reasonable for an eventual active cell of 3.2 in^3 size to be discharged at a 400 ma rate. One fact to forcibly emerge from this matrix was that the 50/50 mixture of benzoyl chloride/1.5M LiAlCl_4 in SOCl_2 , to date the only electrolyte to show reasonable storability, could not support a discharge rate leading to a 400 ma discharge rate cell.

8.5 Benzoyl Electrolyte Rate Investigation

To investigate the possibility of increasing the rate carrying capability of benzoyl chloride-based electrolyte without sacrificing storability, a matrix of storage ampoules and glass test cells was set up, based on the premise that the low rate capability of 1.5M LiAlCl_4 in benzoyl chloride, diluted 50% with thionyl chloride, was caused by low salt concentration. To this end, the following solutions were prepared in a glove box using vacuum-oven dried salts:

Solution I - 2:1 $\text{AlCl}_3/\text{LiCl}$ mole ratio in SOCl_2

Solution II - 1.5M LiAlCl_4 w/10% excess LiCl in SOCl_2

Solution III - 1.25M LiAlCl_4 w/10% excess LiCl in benzoyl chloride

Solution IV - 1.25M LiAlCl_4 w/10% excess LiCl in 50/50 mixed
benzoyl and thionyl chloride

An ampoule storage matrix was prepared from these solutions as follows:

	<u>Ampoule</u>	Soln.	Soln.	Soln.	Soln.
		<u>I</u>	<u>II</u>	<u>III</u>	<u>IV</u>
	A	-	100%	-	-
	B	-	-	100%	-
	C	-	-	-	100%
	D	100%	-	-	-
Storage at +60°C	E	-	50%	50%	-
	F	-	10%	90%	-
	G	-	90%	10%	-
	H	-	Diluted w/ 50% pure benzoyl -		-
	I	-	-	Diluted w/ 50% pure SOCl ₂	
	J	-	80%	20%	-
	K	-	70%	30%	-

Ampoule A, containing 1.5M LiAlCl₄ w/10% excess LiCl in SOCl₂ and calcium, showed edge corrosion within 24 hours. The calcium corroded in two within 168 hours.

Ampoule B, containing 1.25M LiAlCl₄ w/10% excess LiCl in benzoyl chloride, developed a murky brown cast to the electrolyte shortly after sealing. Within 168 hours the calcium metal showed tarnish. By 42 days of storage, the electrolyte had turned to a black hue, with no additional calcium change. After 2 months of storage, no further changes had taken place.

Ampoule C, which contained 1.25M LiAlCl₄ w/10% excess LiCl dissolved in mixed 50/50 benzoyl and thionyl chloride, was a clear light yellow color after ampoule sealing. The calcium showed tarnish within 24 hours of storage. Within 168 hours the calcium showed slight possible edge corrosion. No further visible change occurred to the calcium after this point. The electrolyte slowly darkened to a "whisky" amber by 42 days of storage, with no further changes occurring to the end of 2 months of storage.

Ampoule D, containing 2:1 AlCl_3 , LiCl and calcium, showed immediate corrosion, with the calcium being essentially completely eaten away within 3 hours.

Ampoule E contained 50/50 solutions II and III with calcium. This mix created a solution 1.375M in LiAlCl_4 , with 10% excess LiCl , in 50/50 benzoyl and thionyl chloride. At the 1.5M level, it was this solution with the LiAlCl_4 dissolved in benzoyl chloride, then diluted 50% with thionyl chloride that had earlier showed good storability in ampoule and small sized (.15 in³) stainless steel cells. This ampoule showed calcium tarnish within 24 hours. Over the next month and one-half, the electrolyte slowly blackened, with the calcium showing no visible change. After 7 weeks of storage, the calcium had calved in two, and showed some small signs of corrosion. A week later, no further change had occurred.

Ampoule F contained 10% Solution II and 90% Solution III. This mix created a solution 1.275M in LiAlCl_4 in 10/90 thionyl chloride/benzoyl chloride. The calcium in this ampoule showed calcium tarnish within 24 hours. By 42 days of storage, the electrolyte had slowly blackened, while the calcium showed no further change. By the end of two months of storage, no further change had occurred.

Ampoule G contained 90% Solution II and 10% Solution III. This mix created a solution 1.475M in LiAlCl_4 w/10% excess LiCl in 90/10 thionyl chloride/benzoyl chloride. Within 24 hours the calcium in this ampoule showed visible edge corrosion. By 168 hours of storage, the corrosion had spread slightly, with a white precipitate suspended in the ampoule. By 2 weeks of storage, the calcium had developed a white coating. By 42 days of storage, the calcium had calved. No further change was observed to the end of the 2 month storage.

Ampoule H contained 50% Solution II diluted with 50% pure benzoyl chloride. This mix created a solution of 0.75M LiAlCl_4 with 10% excess LiCl in 50/50 thionyl chloride and benzoyl chloride. This mix was the reverse of the electrolyte used in the previous benzoyl chloride electrolytes, in that here the salt was dissolved in the thionyl, then diluted with benzoyl, rather than the reverse. The calcium in the ampoule showed partial tarnishing within 24 hours and was completely tarnished within 168 hours. The electrolyte, which after sealing had been clear and colorless, slowly began to change, staying clear but becoming a light brown hue by 42 days of storage. A week later, the calcium had calved in three. No further changes had occurred a week later at the end of the 2 month storage.

Ampoule I contained 50% Solution III diluted 50% with pure thionyl chloride. This mix created a solution of .625M LiAlCl_4 w/10% excess LiCl in 50/50 thionyl and benzoyl chloride. Although the previous solutions had been .75M in LiAlCl_4 , this solution was prepared identically to the electrolyte used in the previous benzoyl cell work showing good storability. After sealing, the electrolyte turned a very light murky brown, with the calcium showing tarnished within 24 hours. Aside from the electrolyte slowly deepening in brown color to a light brown, no other visible change occurred to the end of the 2 month storage.

Ampoule J contained 80% Solution II and 20% Solution III. This mix created a solution 1.25M in LiAlCl_4 with 10% excess LiCl in 80/20 thionyl chloride/benzoyl chloride. The calcium in the ampoule showed edge corrosion within 24 hours and severe corrosion by 168 hours.

Ampoule K contained 70% Solution II and 30% Solution III. This mix created a solution 1.425M in LiAlCl_4 with 10% excess LiCl in 70/30 thionyl chloride/benzoyl chloride. The calcium in the ampoule showed severe edge corrosion within 24 hours and general severe corrosion within 72 hours.

In line with earlier work, then, LiAlCl_4 in SOCl_2 (Ampoule A) produced rapid corrosion, while LiAlCl_4 in benzoyl chloride, diluted with thionyl chloride 50%, (Ampoule I) remained stable for prolonged periods. When the salt level in benzoyl chloride was raised (Ampoule B), storability remained good. When the salt level in 50/50 thionyl benzoyl chloride was raised (Ampoules C and E), storability was compromised. High salt solutions containing more than 50% thionyl (Ampoules G, J, K) showed serious corrosion. From the ampoule results, then, raising the salt level in the mixed electrolyte did not appear promising from a storage standpoint, as increasing the salt concentration in the 50/50 mixed electrolyte rendered storability marginal, and using increasing thionyl percentages in the mixed electrolyte seriously degraded storability.

8.6 Enhanced Salt Test Cell Matrix

A glass test cell matrix was constructed using the electrolytes utilized in the preceeding storability matrix. Cathodes were Shawinigan carbon with 15% TFE, of pasted/baked construction. Data and results from the glass cell matrix are given in Table 39.

The enhanced electrolyte salt concentration in the mixed thionyl/benzoyl electrolytes showed enhanced utilization over the 0.75M salt concentration used in the earlier matrices. The best results were obtained with 1.5M LiAlCl_4 in SOCl_2 mixed 70/30 with 1.25M LiAlCl_4 in benzoyl (Ampoule K). At .323 Ah/cm³ average cathode matrix utilization, this is only approximately two-thirds of the performance of 1.5M LiAlCl_4 in SOCl_2 . Of the electrolytes prepared with a 50/50 thionyl to benzoyl ratio, the 1.5M LiAlCl_4 in SOCl_2 mixed with the 1.25M

TABLE 39 - ENHANCED SALT CELL MATRIX

	<u>Trial 1</u>	<u>Trial 2</u>	<u>Trial 1</u>	<u>Trial 2</u>	<u>Trial 1</u>	<u>Trial 2</u>
Electrolyte	50/50 mixed plus 1.25M LiAlCl ₄ (Ampoule C)		1.5M LiAlCl ₄ /SOCl ₂ + 1.25M LiAlCl ₄ /ben. mixed 50/50 (Ampoule E)		1.5M LiAlCl ₄ /SOCl ₂ + 1.25M LiAlCl ₄ / benzoyl mixed 90 SOCl ₂ /10b. (Ampoule G)	
Ohms Load	350		350		350	
Hrs. Discharge Time	2	3½	6.25	8.75	8.25	10.25
OCV	2.46	2.47	2.52	2.52	2.7	2.7
\bar{V}	2.05	2.12	2.13	2.15	2.48	2.43
A-Hr/CM ³	0.048	0.084	0.152	0.216	.232	.284

	<u>Trial 1</u>	<u>Trial 2</u>	<u>Trial 1</u>	<u>Trial 2</u>
Electrolyte	1.5M LiAlCl ₄ /SOCl ₂ 1.25M LiAlCl ₄ /ben mixed 80 SOCl ₂ /20b. (Ampoule J)		1.5M LiAlCl ₄ /SOCl ₂ 1.25M LiAlCl ₄ /b. mixed 70/30 (Ampoule K)	
Ohms	350		350	
Hrs. Discharge Time	11.5	11.5	11.5	12.25.
OCV	2.68	2.68	2.64	2.65
\bar{V}	2.42	2.43	2.39	2.37
A-Hr/CM ³	0.318	0.319	.314	.332

LiAlCl_4 in benzoyl performed best, at an average cathode matrix utilization of 0.184. One interesting result to appear from the matrix, though hardly conclusive from such limited testing, was that the electrolytes made by mixing the salts in the solutes separately, then combining the solutions (Ampoule E), far outperformed the electrolyte made by mixing the solutes and then dissolving the salts (Ampoule C).

8.7 $\text{Ca}(\text{AlCl}_4)_2$ Electrolyte Study

A matrix of storage ampoules and test cells was constructed to check the earlier storage results obtained with $\text{Ca}(\text{AlCl}_4)_2/\text{SOCl}_2$ electrolyte and to determine capacity of the electrolyte against calcium in glass test cells.

A high purity AlCl_3 obtained from Witco Chemical and was dissolved in Kodak SOCl_2 at a 0.75M level. Fluka CaCl_2 was ground to powder in the glove box, weighed, and added to the solution at a 0.75M level plus a 20% excess. Intense bubbling noted on the addition of the CaCl_2 indicated the material had picked up considerable moisture during storage. To enhance the dissolution rate of the CaCl_2 , the electrolyte was refluxed in the glove box for a period of $2\frac{1}{2}$ days. It was then filtered, to remove undissolved CaCl_2 , then was distilled. 280 ml of SOCl_2 had been utilized, while salt amounts were added based on a 250 ml volume. This allowed 30 ml to be distilled over while arriving at the correct final volume. Infrared data was used to monitor the quality of the electrolyte. IR Spectrum 1, Figure 32, shows the condition of the electrolyte prior to distillation. The 2800 and 3500 cm^{-1} area bands, as expected, showed considerable water contamination. After distillation, the distillate, Spectrum 2, Figure 33, showed considerable water contamination species, as expected. Spectrum 3, Figure 34, shows the electrolyte after distillation. While still present, water contamination bands have been reduced considerably.

SPECTRUM NO. 2
DATE 3/22/85
SAMPLE 0.75 M Ca(AlCl₄)₂
in thionyl-
chloride, undistilled
SOURCE Fluka C-62
ultrapure
AlCl₃ refluxed
2 1/2 days

PATH 10 mm quartz
SOLVENT _____
CONCENTRATION _____
PHASE _____
COMMENTS run
against air (empty
cell)
ANALYST ROT

INFRARED
SPECTROPHOTOMETER

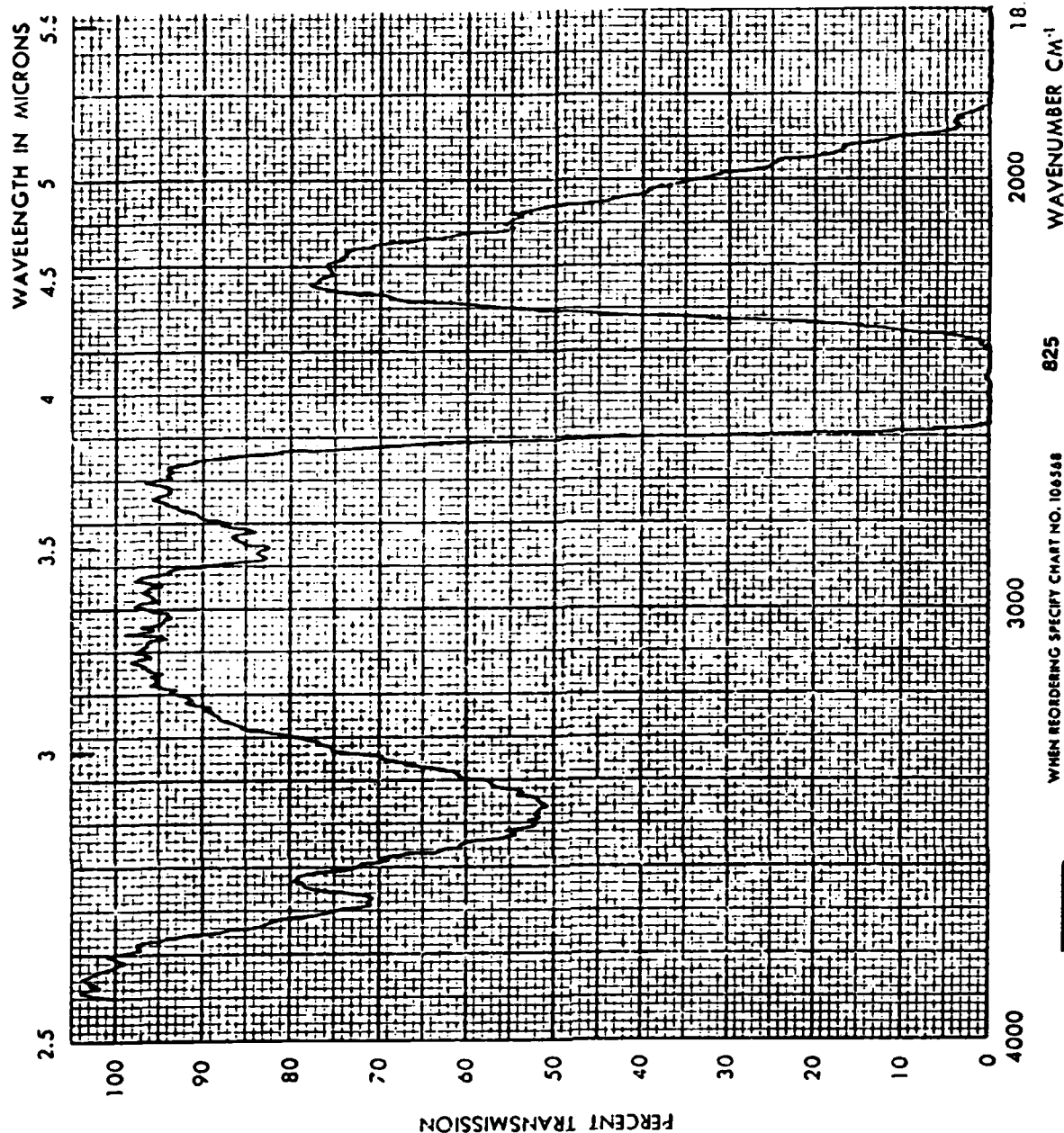


FIGURE 32 - IR Scan - Refluxed 0.75 M Ca(AlCl₄)₂/SOCl₂

SPECTRUM NO. 2
 DATE 3/25/85
 SAMPLE Distillate (simple)
from 0.75M Ca(AlCl₄)₂
in SOCl₂
 SOURCE _____
 STRUCTURE _____
see spectrum 1 into

PATH 10 mm quartz
 SOLVENT _____
 CONCENTRATION _____
 PHASE _____
 COMMENTS run against
air (empty quartz
sample container)
 ANALYST RTC

INFRARED
 SPECTROPHOTOMETER

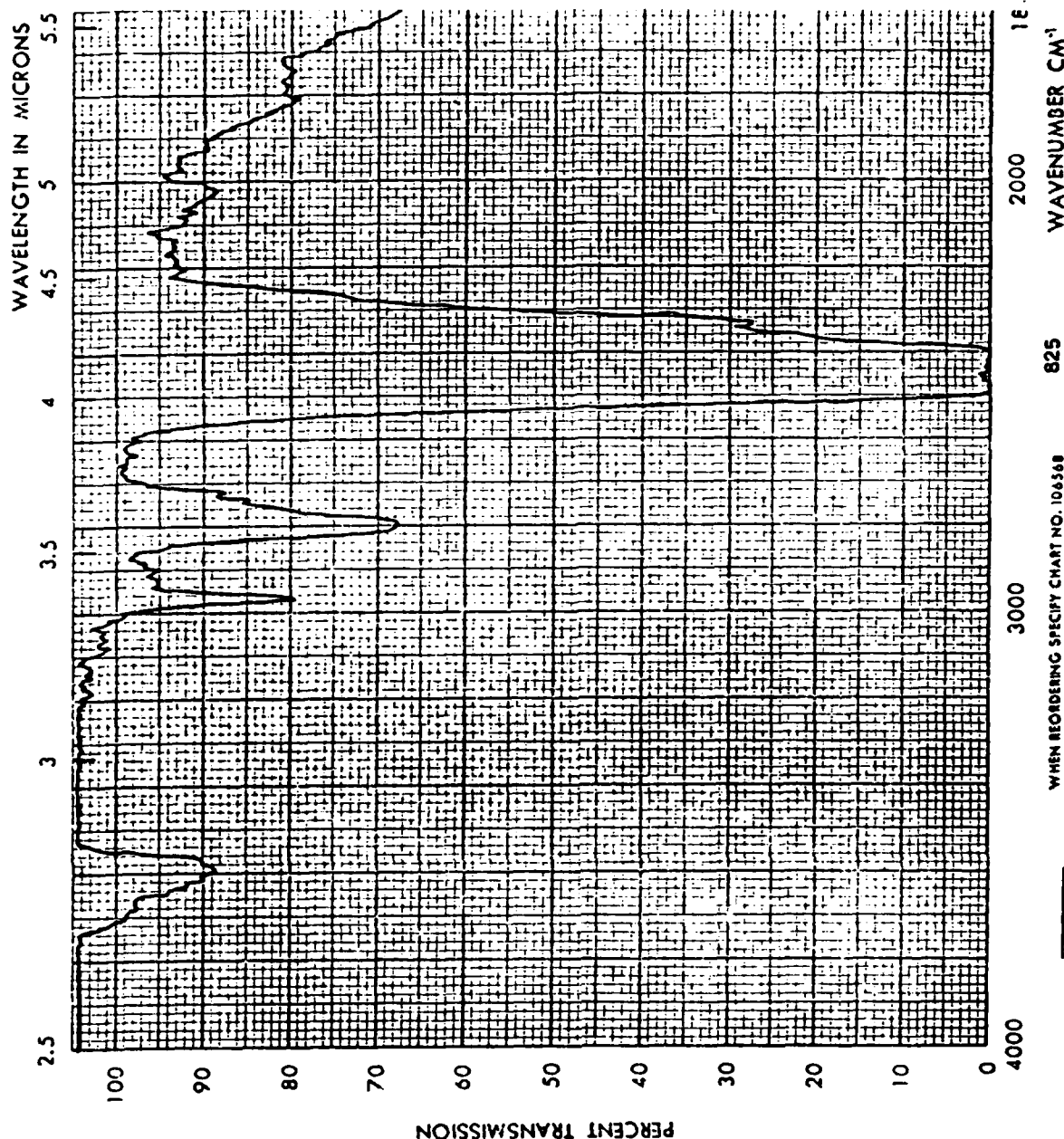


FIGURE 33 - IR Scan - 0.75 M Ca(AlCl₄)₂ Distillate

SPECTRUM NO. 3
 DATE _____
 SAMPLE Pot Lignar
after 30 ml distilled
away from influrid
 SOURCE Ca(AlCl₄)₂ in SOCl₂
 STRUCTURE _____
see Spectrum 1 Info.

PATH 10 mm quartz
 SOLVENT _____
 CONCENTRATION _____
 PHASE _____
 COMMENTS run against
empty quartz
sample holder
 ANALYST _____

INFRARED
 SPECTROPHOTOMETER

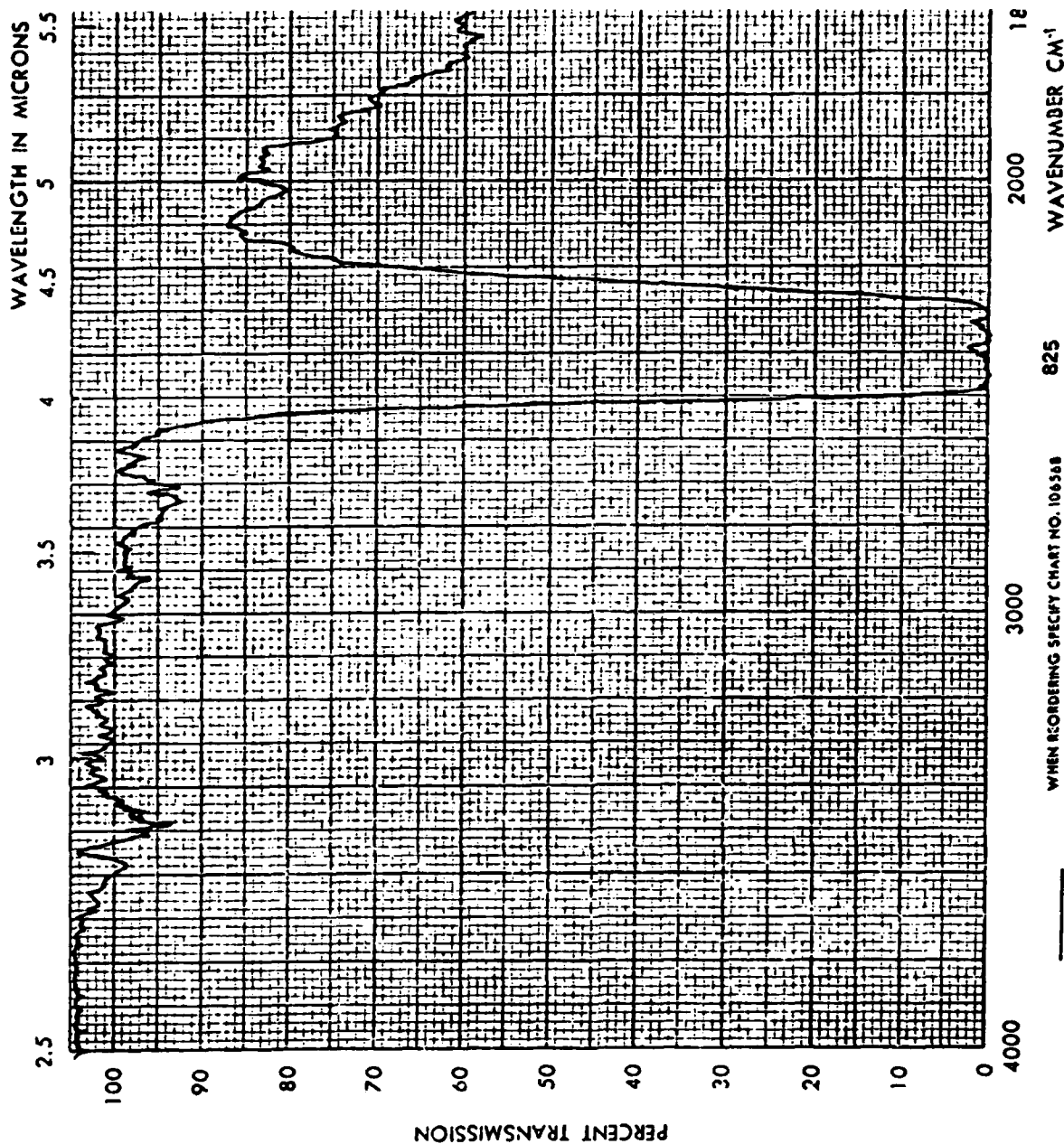


FIGURE 34 - IR Scan - 0.75 M Ca(AlCl₄)₂ After Distilling

Two storage ampoules were made up from the distilled $0.75\text{M Ca(AlCl}_4)_2$ / SOCl_2 electrolyte. Held at 60°C , both ampoules showed corrosion areas within 1 week. By the end of 2 weeks the corrosion had accelerated so that the calcium strips were half eaten away by the end of the third week. The performance of this electrolyte was evaluated in glass test cells with results as shown in Table 40.

TABLE 40 - PERFORMANCE OF $\text{Ca(AlCl}_4)_2$ ELECTROLYTE

Glass Cell No:	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>
Cathode type	-10% TFE Shawinigan -			7.5% TFE Bl.Pearls		
Cath. Thickness, inches	.043	.043	.013	.013	.013	.013
\bar{V}	2.78	2.81	2.7	2.63	2.61	2.65
Load	350	350	350	350	350	350
Hrs. Discharge	18	18	8	8	9.5	7.5
AHr/cm ³	.536	.536	.759	.739	.899	.722
ma/cm ²	1.68	1.68	1.68	1.47	1.47	1.47
Electrolyte used:	0.75M $\text{Ca(AlCl}_4)_2$ in thionyl chloride					

The cathode utilization rate of the thin 7.5% TFE Black Pearls cathodes was the best seen to date. With the utilization rate of the 10% TFE .043" thick Shawinigan cathodes exceeding that produced by LiAlCl_4 - based electrolyte.

A second series of test cells was initiated to check the cathode matrix utilization using thicker electrodes with the $0.75\text{M Ca(AlCl}_4)_2$ in thionyl chloride and to try out a somewhat modified cathode fabrication procedure. The cathode fabrication procedure was modified by using a high pressure (5000 psi) pressing of the cathodes after bakeout to see if density and surface uniformity could be increased without degrading performance. In Table 41 are the results of the glass test cells:

TABLE 41 - $\text{Ca}(\text{AlCl}_4)_2$ ELECTROLYTE/CATHODE STUDY

Cell No.	<u>7</u>	<u>8</u>	<u>9</u>	<u>10</u>
Electrolyte	0.75M($\text{Ca}(\text{AlCl}_4)_2$)		1.5M LiAlCl_4	
Cathode Type	7.5% TFE Bl.Pearls		7.5% TFE Bl.Pearls, pressed after baking	
Cathode Thickness, inches	.038	.038	.040	.040
OCV	2.86	2.86	2.75	2.75
Ohms Load	350	350	350	350
Hrs. discharge	15.5	14.75	11.25	11.75
\bar{V} 2.66	2.67	2.64	2.63	
AHr/cm ³	0.522	0.478	0.33	0.372
ma/cm ²	1.59	1.59	1.57	1.57

As expected with the thicker Black Pearls cathodes, matrix utilization fell off somewhat. Utilization rates with both the Black Pearls and Shawinigan carbons have proven to be quite comparable.

The low utilization (av. = 0.35) of the cathodes in the second series, cells 9 and 10, shows pressing the cathodes after baking to be a less than satisfactory method of improving cathode utility. Standardizing the cathode producing technique proved necessary, as the comparatively grainy Black Pearls 2000 carbon, while performing well, has seemed to be very sensitive to variations in production technique.

Based on the dimensions of the 3.2 in³ stainless steel D-cell utilized for full-sized cell testing, optimum cathode thickness, balancing utilization rates with cell stack packaging efficiency, appeared to fall in the .030" thick area.

A second batch of $\text{Ca}(\text{AlCl}_4)_2/\text{SOCl}_2$ electrolyte was prepared. This was made up to be 1.2 molar. Rather than refluxing to dissolve the salts, this batch of electrolyte was prepared by stirring the salts in the SOCl_2 for 2 days. I-R spectrum 11, given as Figure 35, shows the condition of the electrolyte after addition and dissolution of the Witco AlCl_3 and 10g of ultrapure Anderson Physics CaCl_2 . The I-R scan shows comparatively large amounts of HCl and hydrated forms to be present. This solution was then simple distilled. IR scan 12, given as Figure 36, shows that while HCl presence was lowered significantly, hydrated forms persist. After addition of the remainder of the needed CaCl_2 , the solution was stirred for 2 days to allow as much of the CaCl_2 to dissolve as possible. The solution was then simple distilled, and filtered to remove the excess CaCl_2 . IR scan 13, given as Figure 37, of the finished electrolyte, shows large amount of HCl and hydrated form contamination still present. Since breakdown of thionyl chloride by water is endothermic, it was tempting to conclude that the heat employed in refluxing the reagent tended to drive this reaction to completion. Whether this supposition is correct, refluxing produced a markedly less contaminated electrolyte, and so was employed with subsequent batches of $\text{Ca}(\text{AlCl}_4)_2$ electrolyte.

The 1.2 molar Ca based electrolyte was evaluated in two series of glass test cells. First, as shown in Table 42, to evaluate performance against cathode thickness and second, as shown in Table 43, versus concentration.

SPECTRUM NO. 11
 DATE 4/16/85
 SAMPLE sufficient white
AlCl₃ to produce 1.2 M
Ca(AlCl₄)₂ + 10g And.
Physisic CaCl₂
 STRUCTURE Ca-SOCl₂
Batch 2

PATH 10 mm
 SOLVENT SOCl₂, Kodak
 CONCENTRATION Boyle 1
 PHASE _____
 COMMENTS _____

 ANALYST Rotc

INFRARED
 SPECTROPHOTOMETER

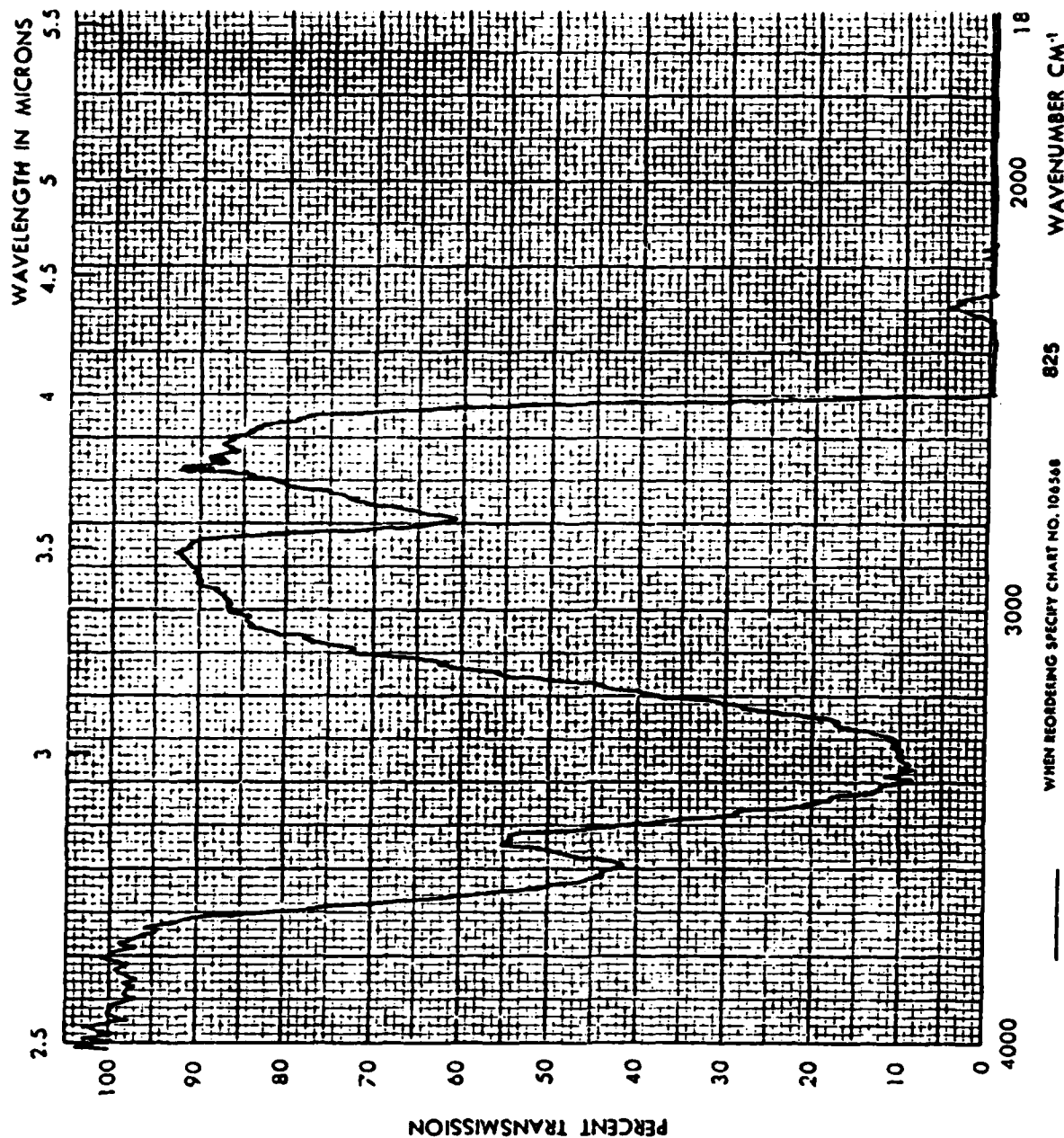


FIGURE 35 - IR Scan - 1.2 M Ca(AlCl₄)₂

SPECTRUM NO. 12
 DATE 4/17/85
 SAMPLE AlCl₃ + small amount C₆H₆ (Batch 2 Ca-SOCl₂) from Spect.
 SOURCE 11 after simple
 STRUCTURE distillation

PATH 10 mm quartz
 SOLVENT _____
 CONCENTRATION _____
 PHASE _____
 COMMENTS run against empty quartz cuvette
 ANALYST ROTC

INFRARED
 SPECTROPHOTOMETER

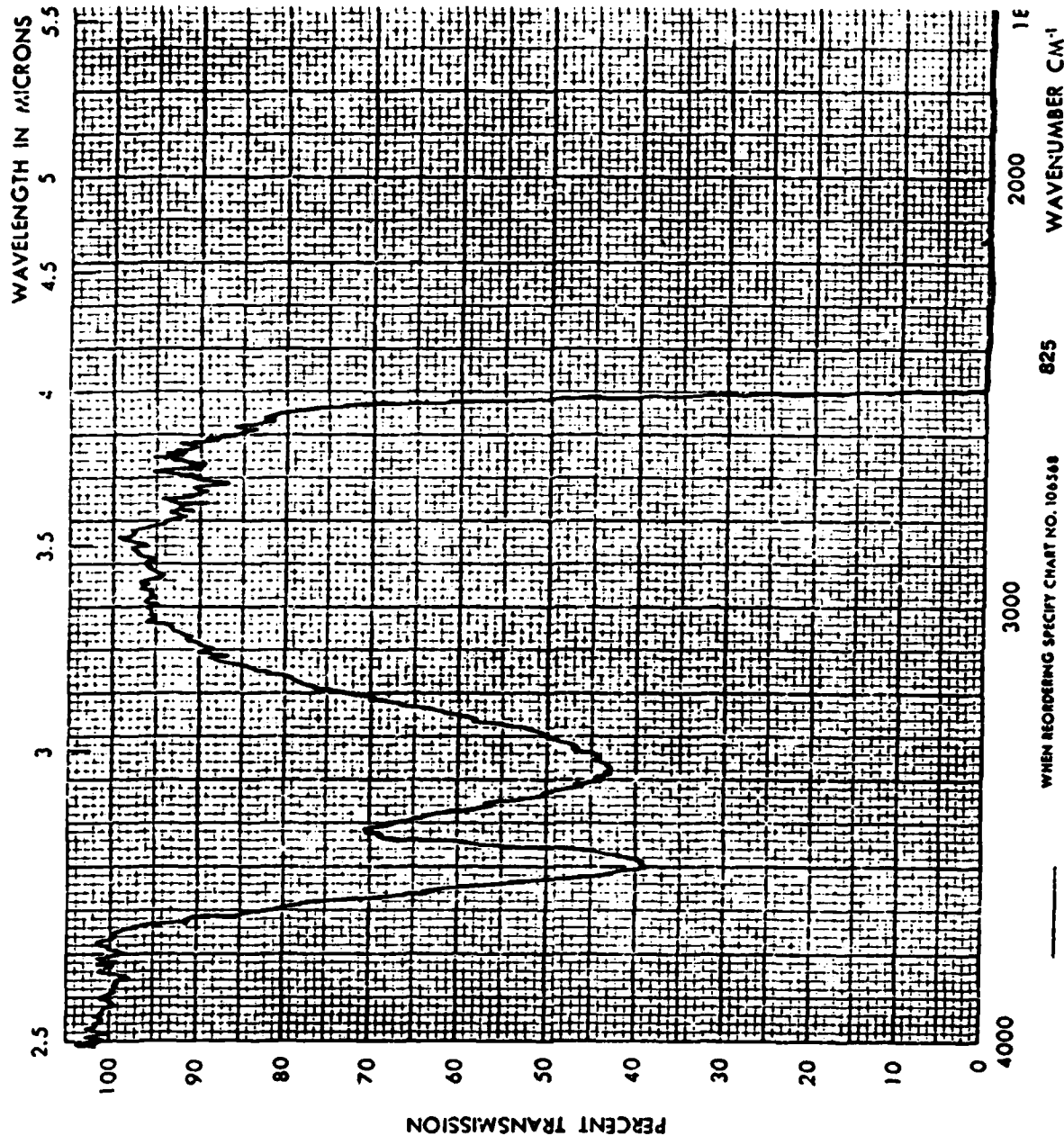


FIGURE 36 - IR Scan - 1.2 M $\text{Ca}(\text{AlCl}_4)_2$ After Distillation

SPECTRUM NO. 13
 DATE 4/19/85
 SAMPLE Batch 2 Ca(AlCl₄)₂
in sol₂ after
distilling & filtering
 SOURCE _____
 STRUCTURE _____

PATH _____ mm
 SOLVENT _____
 CONCENTRATION _____
 PHASE _____
 COMMENTS run against
empty quartz cell
 ANALYST ROC

INFRARED
 SPECTROPHOTOMETER

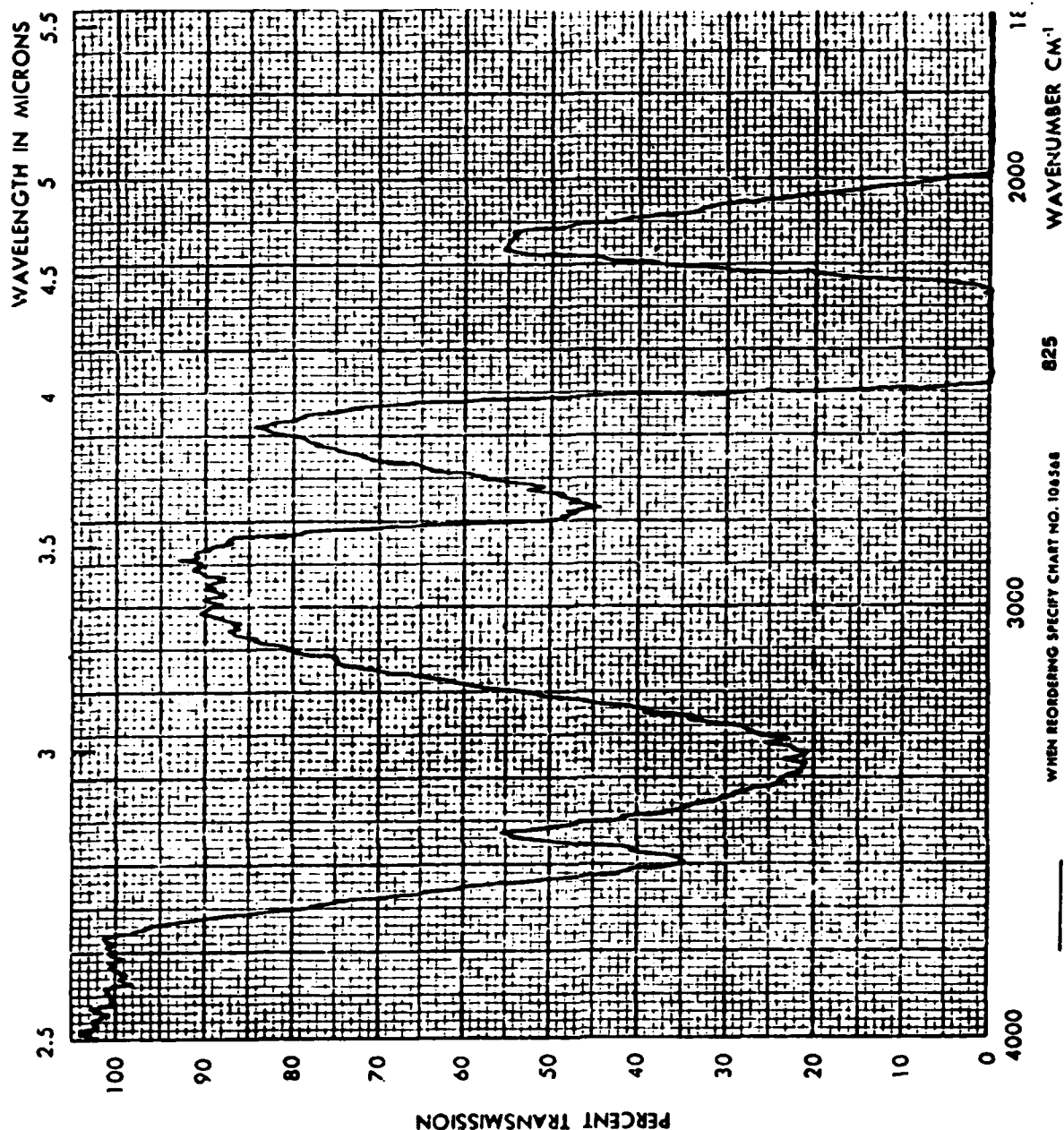


FIGURE 37 - IR Scan - 1.2 M Ca(AlCl₄)₂, Distilled & Filtered

TABLE 42 - PERFORMANCE VS CATHODE THICKNESS

Cell No.	<u>13</u>	<u>14</u>	<u>15</u>	<u>16</u>	<u>17</u>	<u>18</u>
Electrolyte	-1.2 molar $\text{Ca}(\text{AlCl}_4)_2/\text{SOCl}_2$					
Cathode type	Bl. Pearls 2000, wet pasted, baked, 7.5% TFE					
Cathode thickness	.032	.032	.037	.037	.012	.012
OCV	2.85	2.85	2.82	2.84	2.83	2.85
\bar{V}	2.74	2.69	2.62	2.65	2.64	2.61
Load ohms	350	350	300	300	480	470
Hours Discharge	15.25	14.75	12.25	13.75	10.5	9
AHr/cm ³	0.613	0.582	0.478	0.54	0.794	0.685
ma/cm ²	1.64	1.61	1.82	1.84	1.15	1.15

TABLE 43 - PERFORMANCE VS CONCENTRATION

Cell No.	<u>19</u>	<u>20</u>	<u>21</u>	<u>22</u>	<u>23</u>	<u>24</u>
Electrolyte	1.2M Ca(AlCl ₄) ₂		1.0M Ca(AlCl ₄) ₂		0.8M Ca(AlCl ₄) ₂	
Cathode type	Bl. Pearls, wet pasted, 10% TFE W/Glass Binder					
Cathode size	-	.685" x .54" x .025" - .				
OCV	2.89	2.89	2.88	2.89	2.87	2.87
\bar{V}	2.7	2.71	2.75	2.75	2.77	2.76
Load ohms	350	350	350	350	350	350
Hrs. Discharge	9	9.25	10.25	10.25	11	11
AHr/cm ³	0.457	0.474	0.533	0.533	0.576	0.574
ma/cm ²	1.61	1.61	1.63	1.63	1.66	1.66

The cathodes used for the cells in Table 43 had an addition made to them. When the dry mix was blended, a piece of .002" thick Manning separator was added, so that the separator material was finely ground and distributed throughout the mix. The mix was then wetted with either water or isopropyl alcohol before being pressed. On evaluation of the resulting cathodes, no perceptible difference was found between the cathodes prepared with isopropyl and with water, so the water-prepared cathodes were utilized. The addition of the glass separator definitely eliminated the cracking that tends to develop when the cathode is dried and baked. The disadvantage to adding the binder was an efficiency reduction in matrix utilization.

In Table 44, below, are reported discharge results for a series of glass test cells made up using the 0.8M $\text{Ca}(\text{AlCl}_4)_2/\text{SOCl}_2$ electrolyte but using cathodes made of Black Pearls 2000 of varying thickness to compare performance with the cells using glass binder-addition cathodes:

TABLE 44 - PLAIN CATHODES COMPARISON

Cell No.	25	26	27	28	29	30
Electrolyte	- 0.8M $\text{Ca}(\text{AlCl}_4)_2/\text{SOCl}_2$ -					
Cathode type	Bl. Pearls, pasted, baked, 7.5% TFE -					
Cath. thickness, inches	.018	.018	.030	.030	.043	.043
\bar{V}	2.6	2.68	2.75	2.77	2.71	2.68
Load Ohms	350	350	350	350	350	350
AHr/cm ³	0.494	0.527	0.572	0.522	0.386	0.469
ma/cm ²	1.55	1.59	1.63	1.66	1.61	1.59

Based on the results of the glass test cells, 0.8M $\text{Ca}(\text{AlCl}_4)_2/\text{SOCl}_2$ electrolyte was chosen for the 50 proof-of-concept cells built.

SECTION IX

PROOF-OF-CONCEPT ACTIVE CELLS

9.1 Proof-Of-Concept Introduction

Fifty 3.2 in³ volume stainless steel, hermetically sealed cells were constructed and discharged. This was to be an optimized cell, using the best configurations of components studied to date, to allow comparison between the as-built cell and the cell goal, 14 A-H life above 2.0 volts above 55°F under a 400 ma discharge rate.

9.2 Active Cell Final Configuration

The cell casing used was 304 stainless steel, of nominal .022 inch thickness, with dimensions of 1.32" x 1.32" x 1.88" tall. The header for the cell was fitted with a glassed-in positive terminal pin, a 150 psi activating vent sticker and a fill tube.

The cell stack consisted of 20 cathodes and 21 anodes. The cathodes were made with Black Pearls 2000 carbon, 10% TFE content, added in the form of DuPont TFE Dispersion Product 30, with Manninglass 1200 separator added to the dry mix in a ratio of 1 in² for every 4 in² of finished nominal .028" thick cathode. The dry mix of carbon and separator was ground in a blender, then suspended in water. The TFE dispersion was added and the mix briefly blended, then vacuum filtered. This step was repeated, and the two resulting half-plates were sandwiched with grid. The grid piece was 5" x 7", with connecting tab material ready spot welded on, the area of spot welded tab extending one-quarter inch onto the grid. The resulting cathode plate was then wet pressed twice between blotter paper at low pressure (250 psi), then pressed between blotter paper at high pressure 2500 psi. The plates were layered between aluminum foil, and tightly jigged between aluminum plates. After a 24 hr. air-drying period, the jigged cathode plates were sintered at 620°F for 20 minutes after cooling.

the plates were cut to finished size, 1" x 1.25" and given a final 72 hr. drying at 165°F in a vacuum oven.

The anodes were made of Pfizer .010" thick calcium. The calcium, which was stored in light mineral oil, was degreased using hexane, then annealed in a vacuum oven at 300°C. The calcium was polished with a stainless steel bristle brush, then cut to final dimension using shears. The grid, the same as used for the cathode collector grid, was Exmet 3Ni3.3-4/0. A small rolling mill was used to embed the grid into the calcium. Grid pieces were cut to 1.2" x 1.4". Calcium was cut to 1.0" x 1.4". After rolling, calcium measured 1.06 - 1.1 x 1.4". This grid overlap left a grid extension of approximately 0.1" inch along the side of the anode to spotweld connector tab.

The separation used was Dexter 255, cut into pieces 3" x 1.25" x .012". The separation was U-wrapped around the cathodes. As may be seen on the cell diagram in Figure 38, the anode tabs were "combed" over and spotwelded to the side of the can, making the cell can-negative. The cathode leads were "combed" to the center of the stack, then attached to the cover pin using a tab lead with accordian pleats folded into it. Finished cell weight averaged 61g.

9.3 Ca Active Cells Proof-Of-Concept Electrolyte

0.8M $\text{Ca}(\text{AlCl}_4)_2/\text{SOCl}_2$ was chosen for use in the Proof-of-Concept active cells. Kodak SOCl_2 , Witco AlCl_3 and Fluka CaCl_2 were utilized for the electrolyte. The high-purity Witco AlCl_3 and the Kodak SOCl_2 were used as received. The Fluka lump CaCl_2 was ground to powder in mortar and pestle in a glove box, then was dried for 16 hours at 450°C in a vacuum oven prior to use. The 0.8M $\text{Ca}(\text{AlCl}_4)_2/\text{SOCl}_2$ was prepared in a glove box in four 750 ml batches. 72g CaCl_2 , to provide an approximately 10% excess, was added to a 1000 ml boiling flask.

APPLICATION		REVISIONS			
NEXT ASSY	USED ON	LTR	DESCRIPTION	DATE	APPROVED

DEXTER 255,
.012 GLASS U-WRAP
SEPARATOR

.010 CALCIUM
ANODE

TEFLON CELL
STACK WRAP

.028 CARBON/TEFLON
CATHODE

ACCORDIAN-PLEAT
CONNECTOR TAB

UNLESS OTHERWISE SPECIFIED
DIMENSIONS ARE IN INCHES
TOLERANCES: FRACTIONS \pm
ANGLES \pm
3 PLACE DECIMALS \pm .010
2 PLACE DECIMALS \pm .00

CONTRACT NO.

DATE

PREPARED BY *M. P. Kelly* 6-17-85

CHECKED

ENGINEER



EAGLE PICHER INDUSTRIES, INC.
COUPLES DEPARTMENT
JOPLIN, MISSOURI



SIZE

A

FSCM

81855

DRAWING NO.

SCALE

~

SHEET

FIGURE 38 - ACTIVE CELL DIAGRAM -131-

250 ml of the Kodak SOCl_2 was added to the flask, then 159.6g of the Witco AlCl_3 . 530 ml of Kodak SOCl_2 was then added. The total of 780 ml of Kodak SOCl_2 was to allow for a final distillation step. Glass boiling chips and a magnetic stir bar were added to the flask, a reflux condenser was set in place and a heating mantle employed to add heat to reflux the electrolyte. Refluxing of the electrolyte was carried out for 16 hours. After cooling, a sample was withdrawn and checked by IR for hydration products and HCl presence. IR spectrum for batch 1 of the electrolyte is given as Figure 39. The reflux condenser was replaced with a distilling head and condenser, and the resulting electrolyte was simple distilled with 30 ml of distillate being brought across. After cooling, a second IR sample was taken and run. The resulting spectrograph is given as Figure 40. The surprising result was that the amounts of hydrated species and HCl had increased with the distilling step.

Batch 2 of the electrolyte was handled in an identical fashion. IR spectrographs of the electrolyte after refluxing and after distillation are given as Figures 41 and 42. Distillation of batch 2 also increased hydrated forms and HCl content. A small portion of the batch 2 electrolyte was spiked with 100 ppm H_2O and then 200 ppm H_2O . IR spectrographs were obtained on both spiked samples and are given as Figures 43 and 44. A standard additions plot was made from the data on the hydrated forms peaks from Figures 42-44. This plot is given as Figure 45. This plot showed the water content of the batch 2 electrolyte after distilling to be approximately 123 ppm.

Because of the unexpected increases in water-related forms on distilling, batches 3 and 4 of the electrolyte were made up and refluxed, but with only 750 ml SOCl_2 , and were not distilled. After reflux IR spectrographs of these batches are given as Figures 46 and 47. As it was the highest batch in water related forms, batch 1 was held in reserve, with batches 2, 3 and 4 being used to activate the cells.

SPECTRUM NO. 44
 DATE 5/15/85
 SAMPLE Proof of Concept
cell 0.8 M Ca(AICl₄)
batch 1 after reflux
 SOURCE _____
 STRUCTURE _____

PATH 10 mm quartz
 SOLVENT _____
 CONCENTRATION _____
 PHASE _____
 COMMENTS run
against empty cell

 ANALYST ROT C

INFRARED
 SPECTROPHOTOMETER

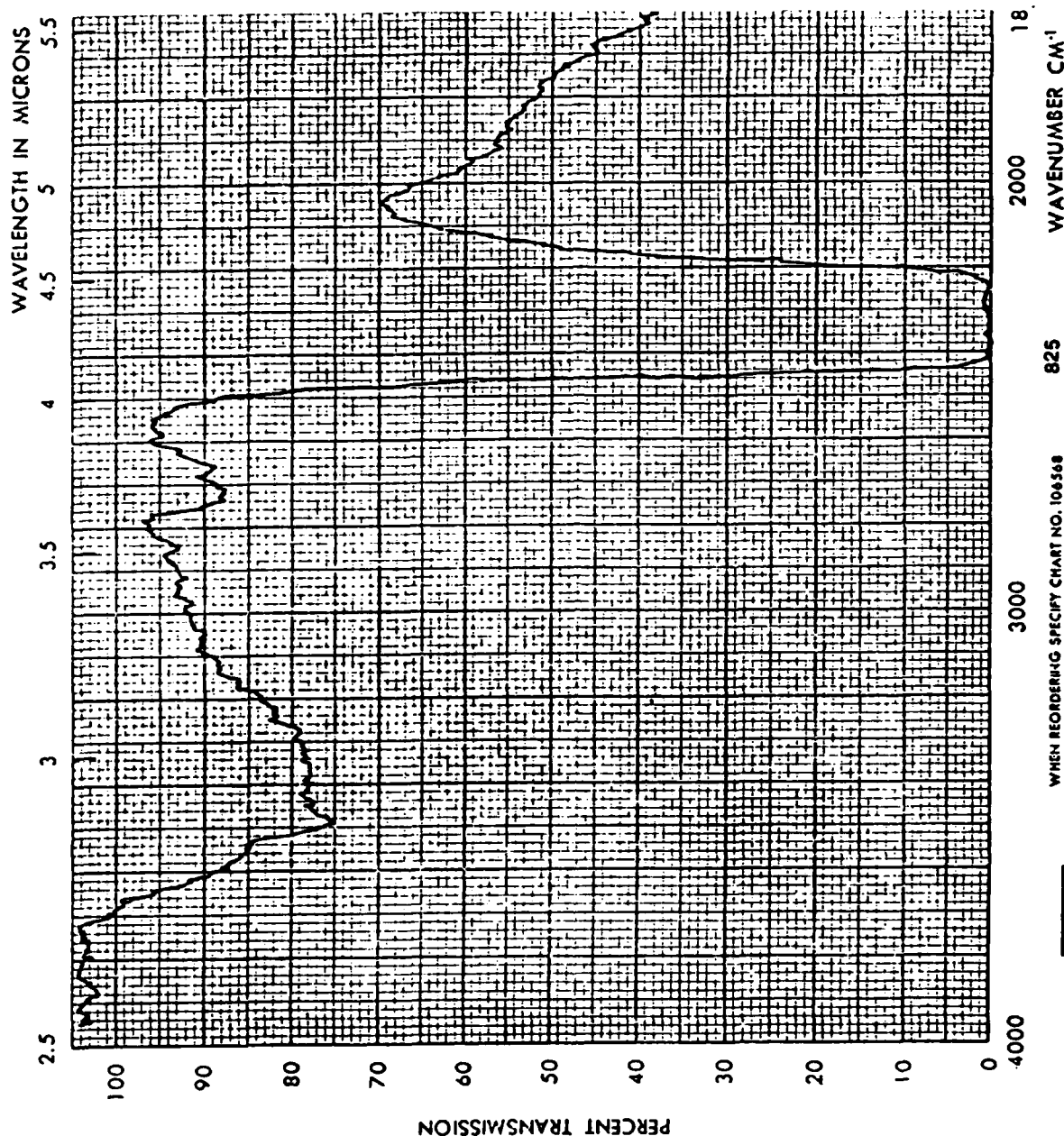


FIGURE 39 - Batch 1 Electrolyte After Reflux

SPECTRUM NO. 15
DATE 5/14/85
SAMPLE Proof of Concept
well 0.8 M Ca(Al₂Si₂O₇)₂
batch 1 after
SOURCE distilling
STRUCTURE _____

PATH 10 mm quartz
SOLVENT _____
CONCENTRATION _____
PHASE _____
COMMENTS run against
empty cell

ANALYST ROT C

INFRARED
SPECTROPHOTOMETER

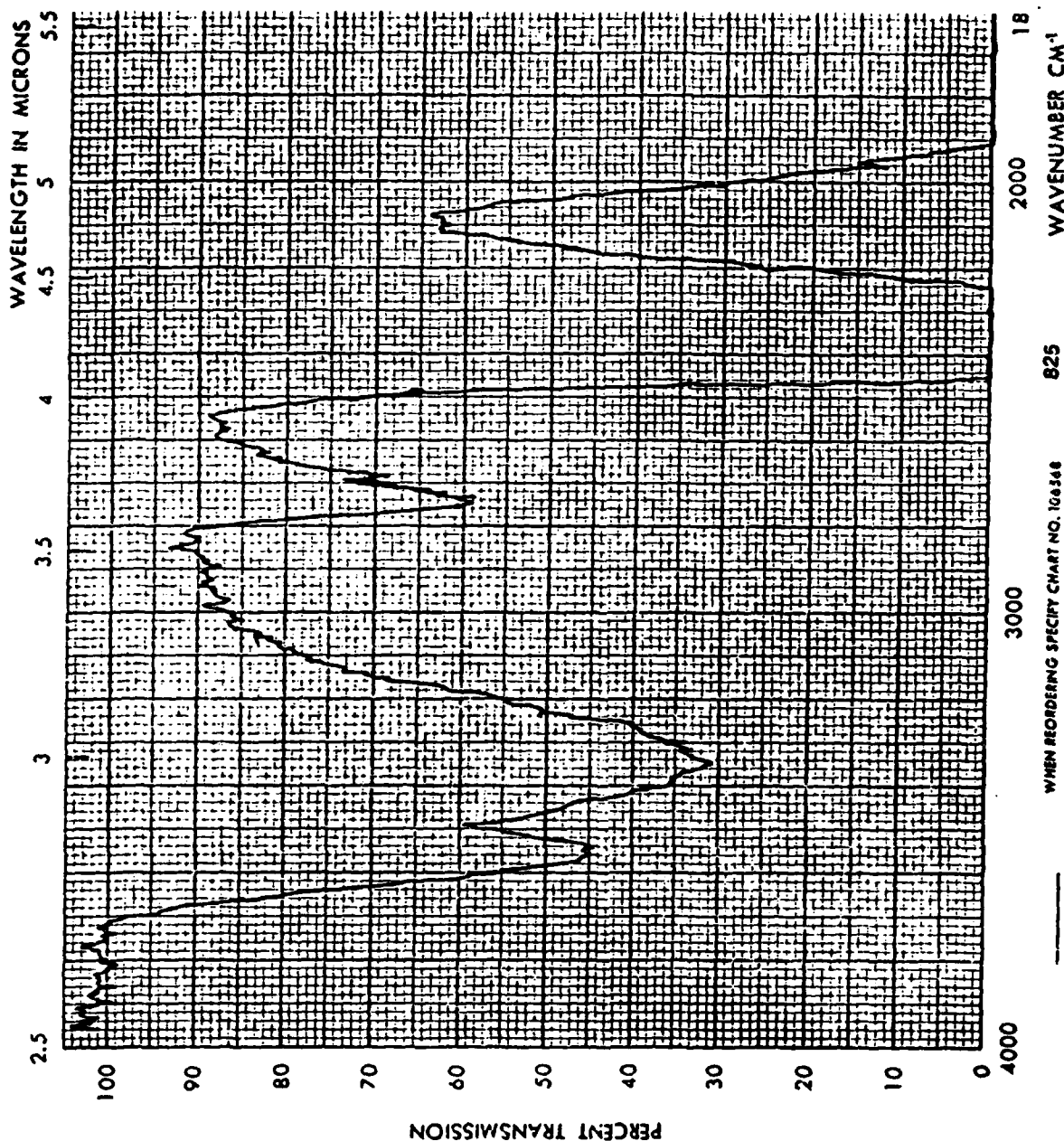


FIGURE 40 - Batch 1 Electrolyte After Distilling

SPECTRUM NO. 16
 DATE 5/17/85
 SAMPLE Proof of Concept
0.8M Ca(AlCl₄)₂
sol, batch 2
 SOURCE after refluxing
 STRUCTURE _____

PATH 10 mm quartz
 SOLVENT _____
 CONCENTRATION _____
 PHASE _____
 COMMENTS run against
empty cell
 ANALYST ROTC

INFRARED
 SPECTROPHOTOMETER

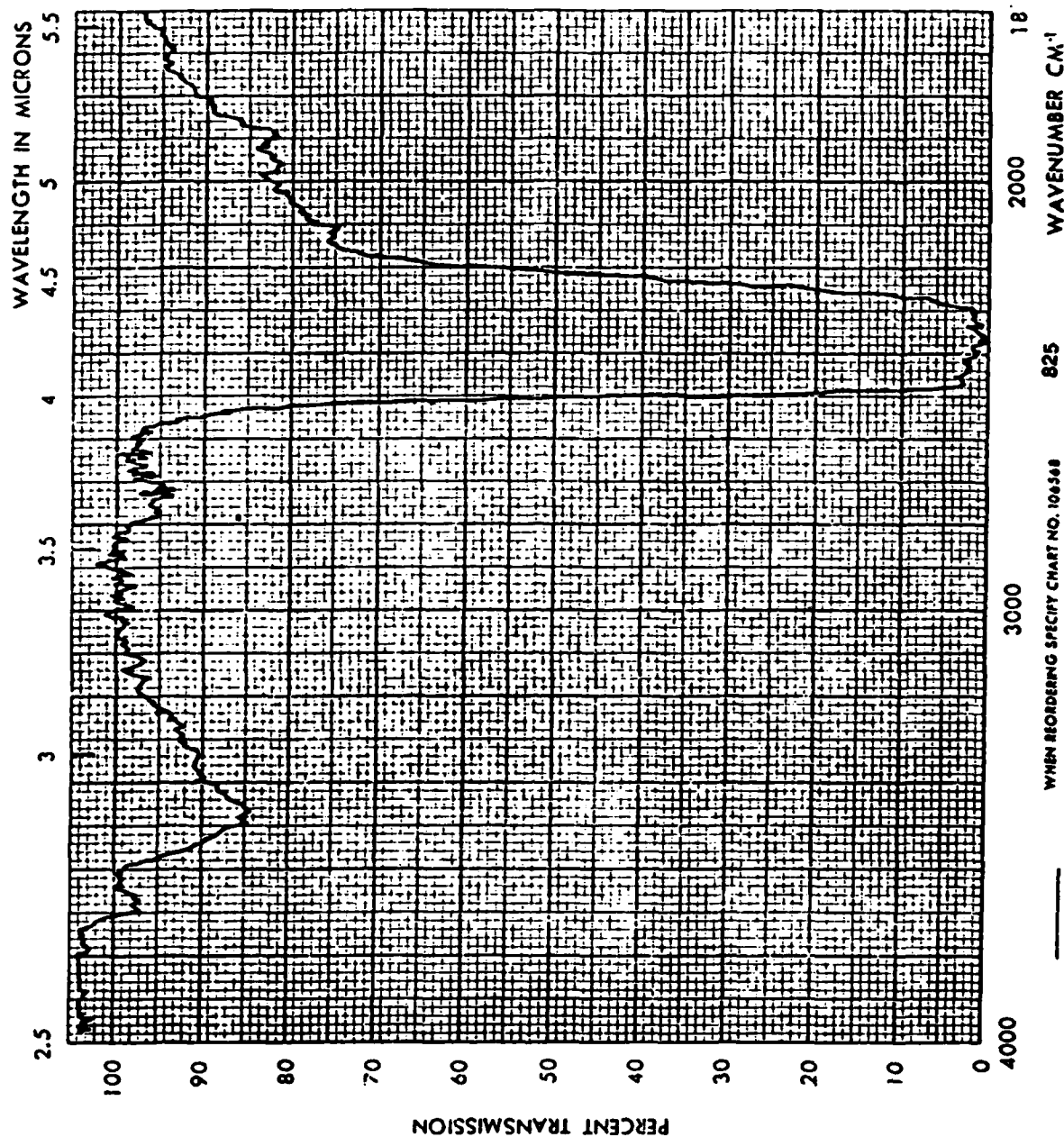


FIGURE 41 - Batch 2 Electrolyte After Reflux

SPECTRUM NO. 17
DATE 5/20/85
SAMPLE 0.8 M Cu(AICl₄)₂
/SOCl₂ for proof
of concept cells
SOURCE after distilling
STRUCTURE Batch 2

PATH 10 mm quartz
SOLVENT _____
CONCENTRATION _____
PHASE _____
COMMENTS run
against empty
cell
ANALYST ROTc

INFRARED
SPECTROPHOTOMETER

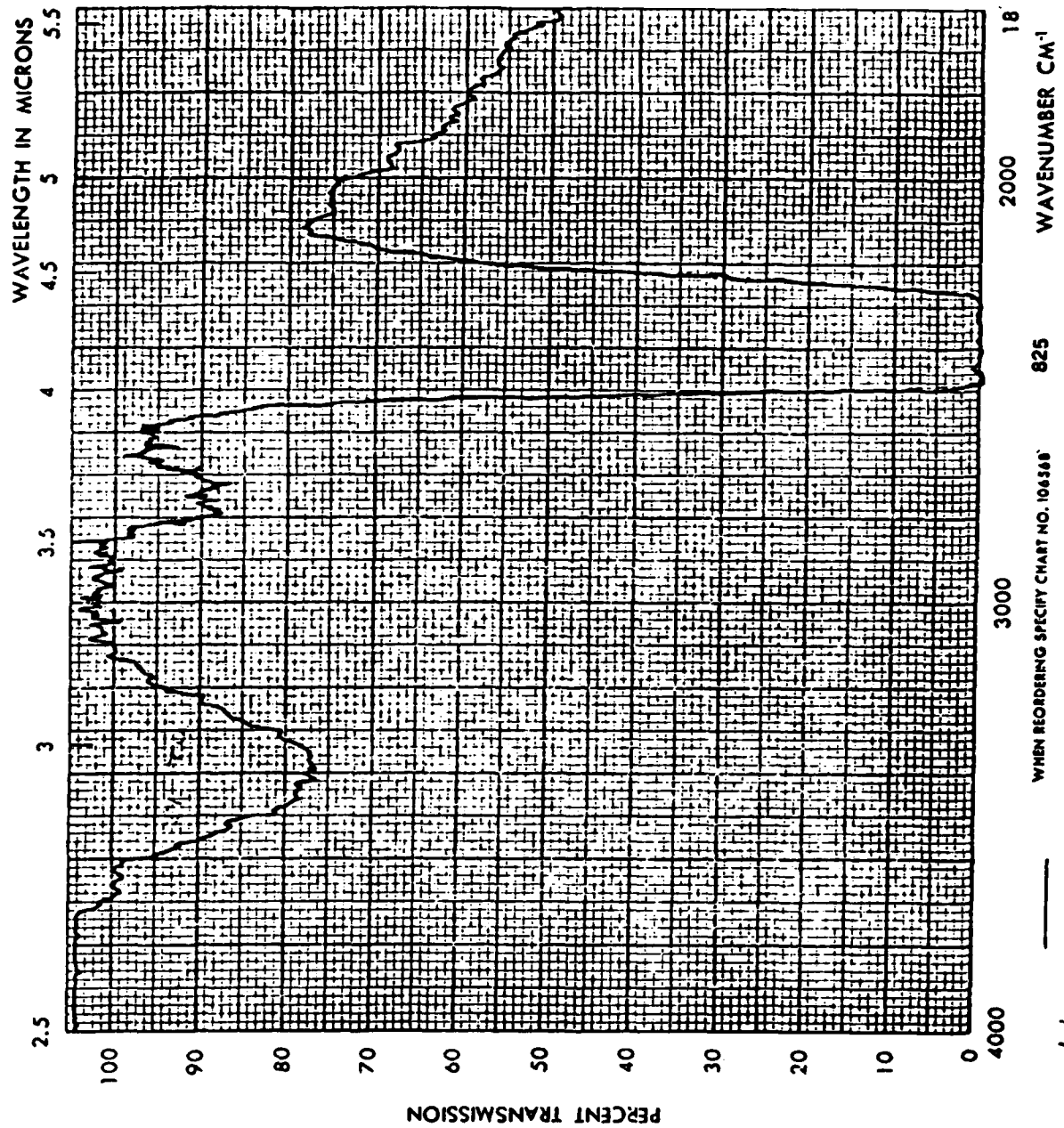


FIGURE 42 - Batch 2 Electrolyte After Distilling

SPECTRUM NO. 18
 DATE 5/20/85
 SAMPLE Batch 2 Proof of
Concept 0.8M
Ca(AlCl₄)₂ spiked
 SOURCE w/ 100 mg/l H₂O
 STRUCTURE _____

PATH 10 mm quartz
 SOLVENT _____
 CONCENTRATION _____
 PHASE _____
 COMMENTS run
against empty
cell
 ANALYST ROT C

INFRARED
 SPECTROPHOTOMETER

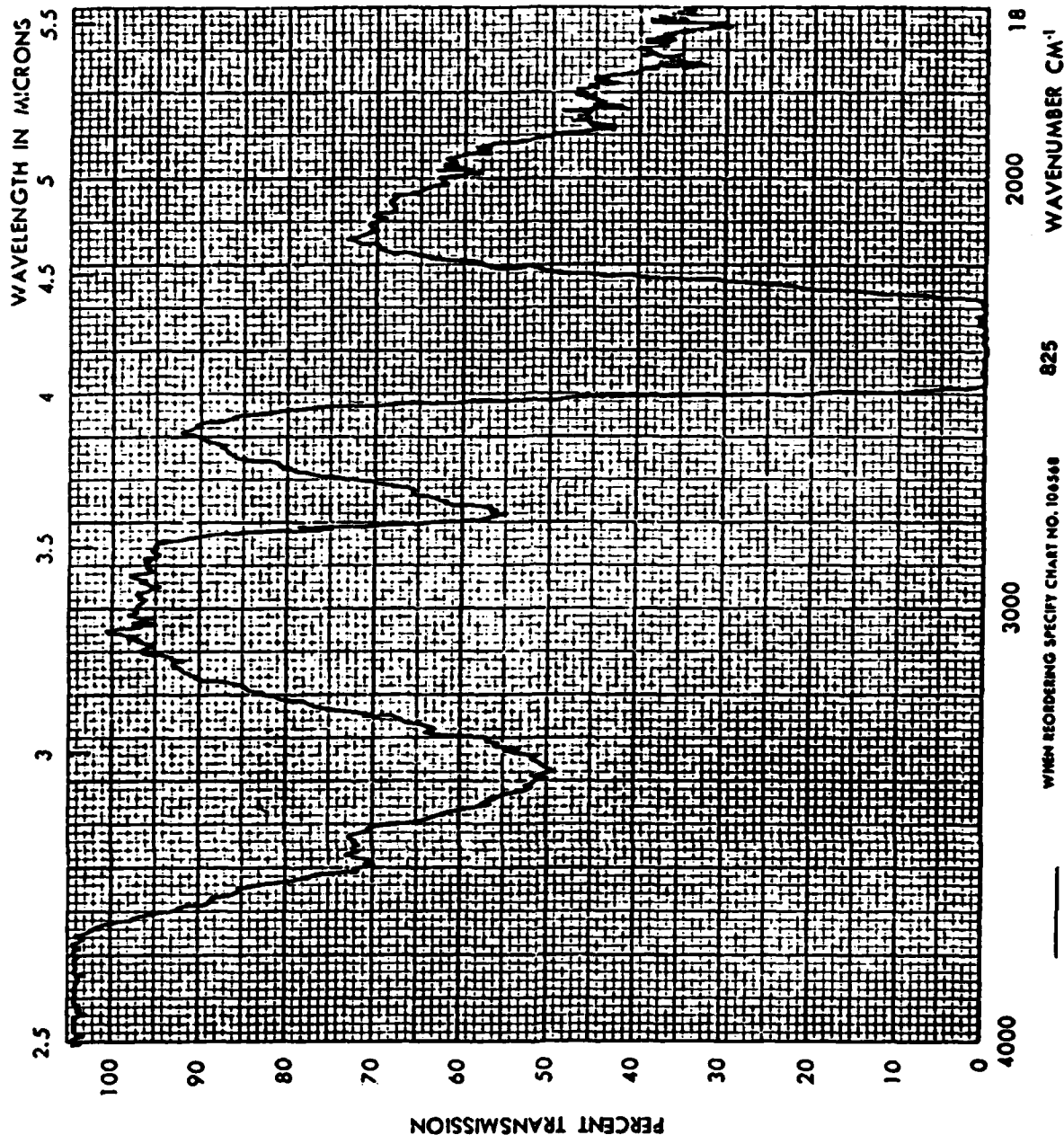


FIGURE 4.3 - Batch 2 Electrolyte w/100 PPM Water

SPECTRUM NO. 19
 DATE 5/29/85
 SAMPLE Batch 2 Proof of
Concept 0.8 M Ca(Ac)₄
1500 Hz electrolyte
 SOURCE Spiked w/ 200
 STRUCTURE 2 ppm H₂O

PATH 10 mm quartz
 SOLVENT _____
 CONCENTRATION _____
 PHASE _____
 COMMENTS run against
empty cell
 ANALYST ROT

INFRARED
 SPECTROPHOTOMETER

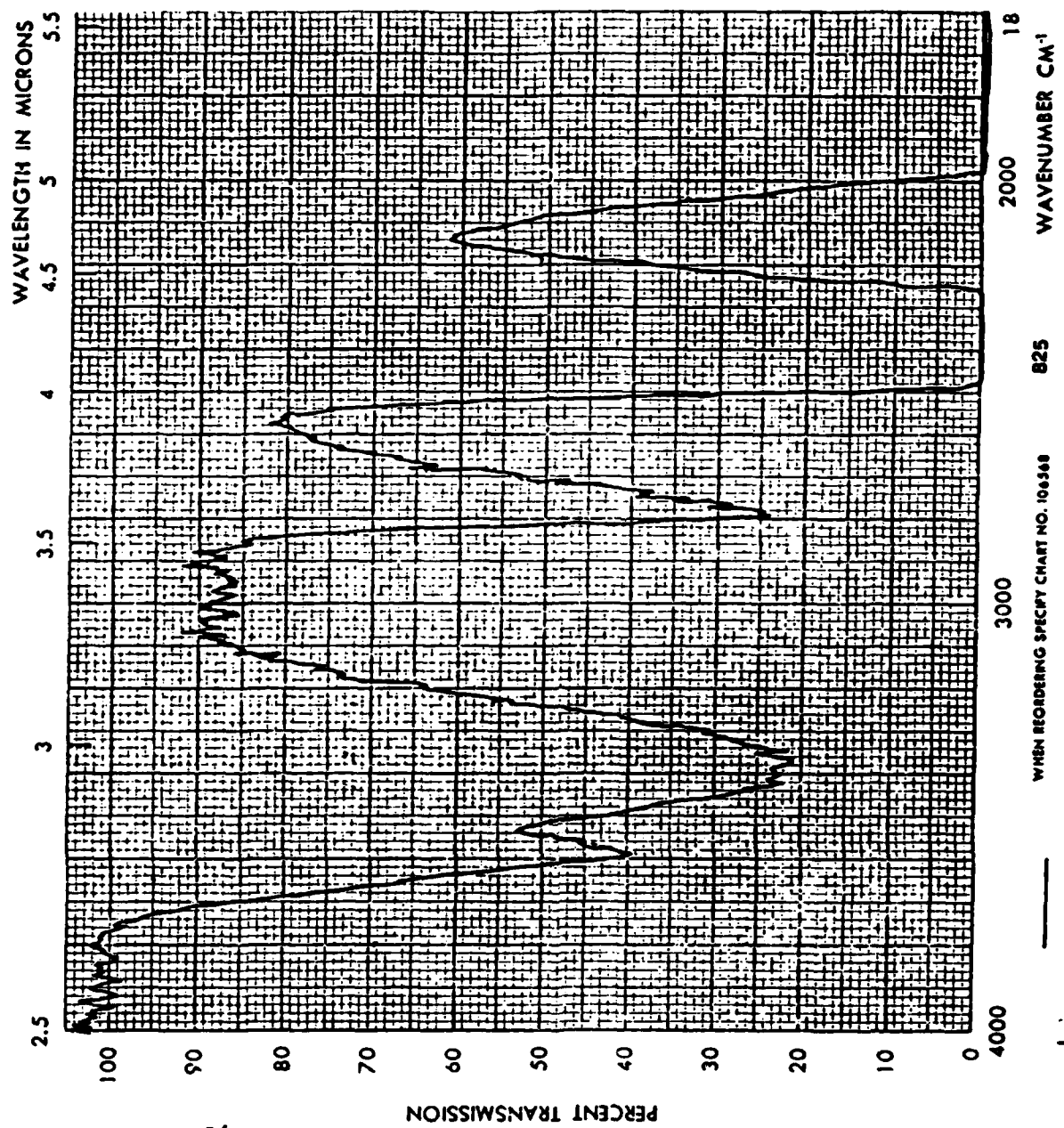


FIGURE 44 - Batch 2 Electrolyte W/200 PPM Water

TRANSMISSION UNITS VS. PPM WATER

FOR: BATCH 2 0.8M $\text{Ca}(\text{AlCl}_4)_2$ ELECTROLYTE

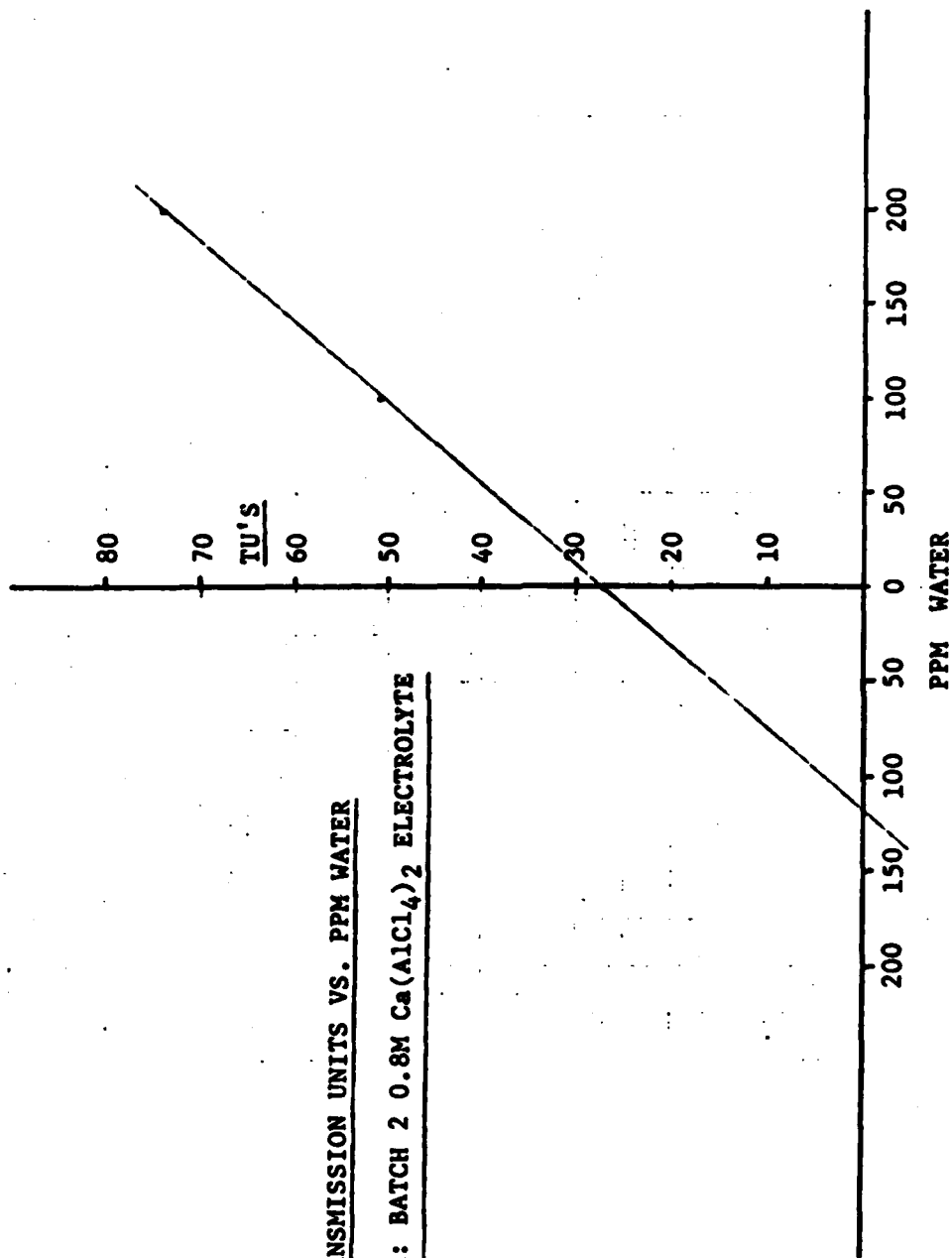


FIGURE 45 Standards Addition Plot - PPM Water

SPECTRUM NO. 5/21/85
 DATE Prod of Concept
 SAMPLE 0.8 M Cs (AlCl₄)
batch 3 after
reflux
 SOURCE _____
 STRUCTURE _____

PATH 10 mm quartz
 SOLVENT _____
 CONCENTRATION _____
 PHASE _____
 COMMENTS run against
empty cell
 ANALYST ROT

INFRARED
 SPECTROPHOTOMETER

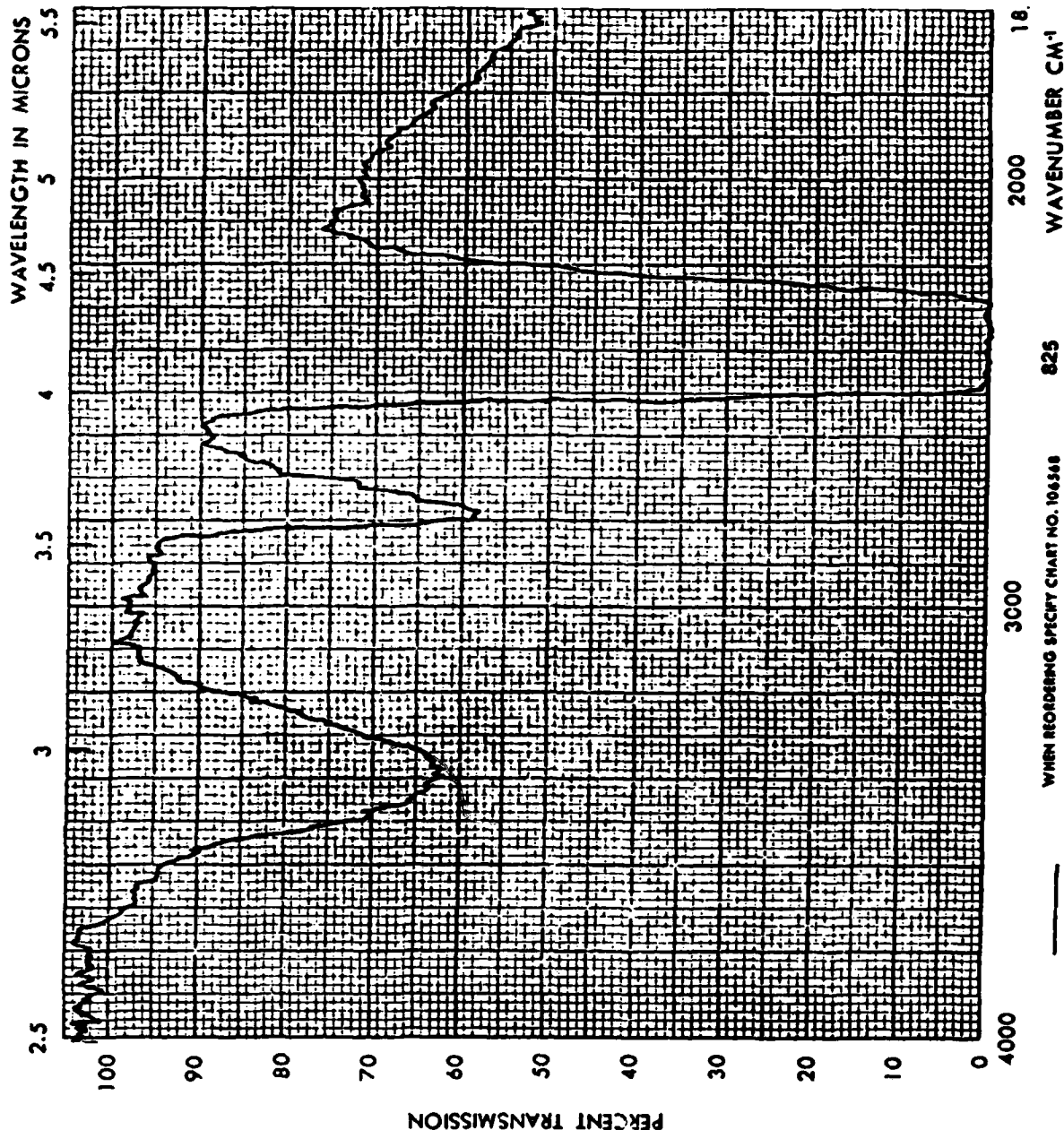


FIGURE 46 - Batch 3 Electrolyte After Reflux

SPECTRUM NO. _____
 DATE 5/22/85
 SAMPLE Proof of Concept
0.8 M Ca(AlCl₄)₂/SOCl₂
Batch 4 after reflux
 SOURCE _____
 STRUCTURE _____
 PATH 10 mm quartz
 SOLVENT _____
 CONCENTRATION _____
 PHASE _____
 COMMENTS _____
 ANALYST ROT

INFRARED
SPECTROPHOTOMETER

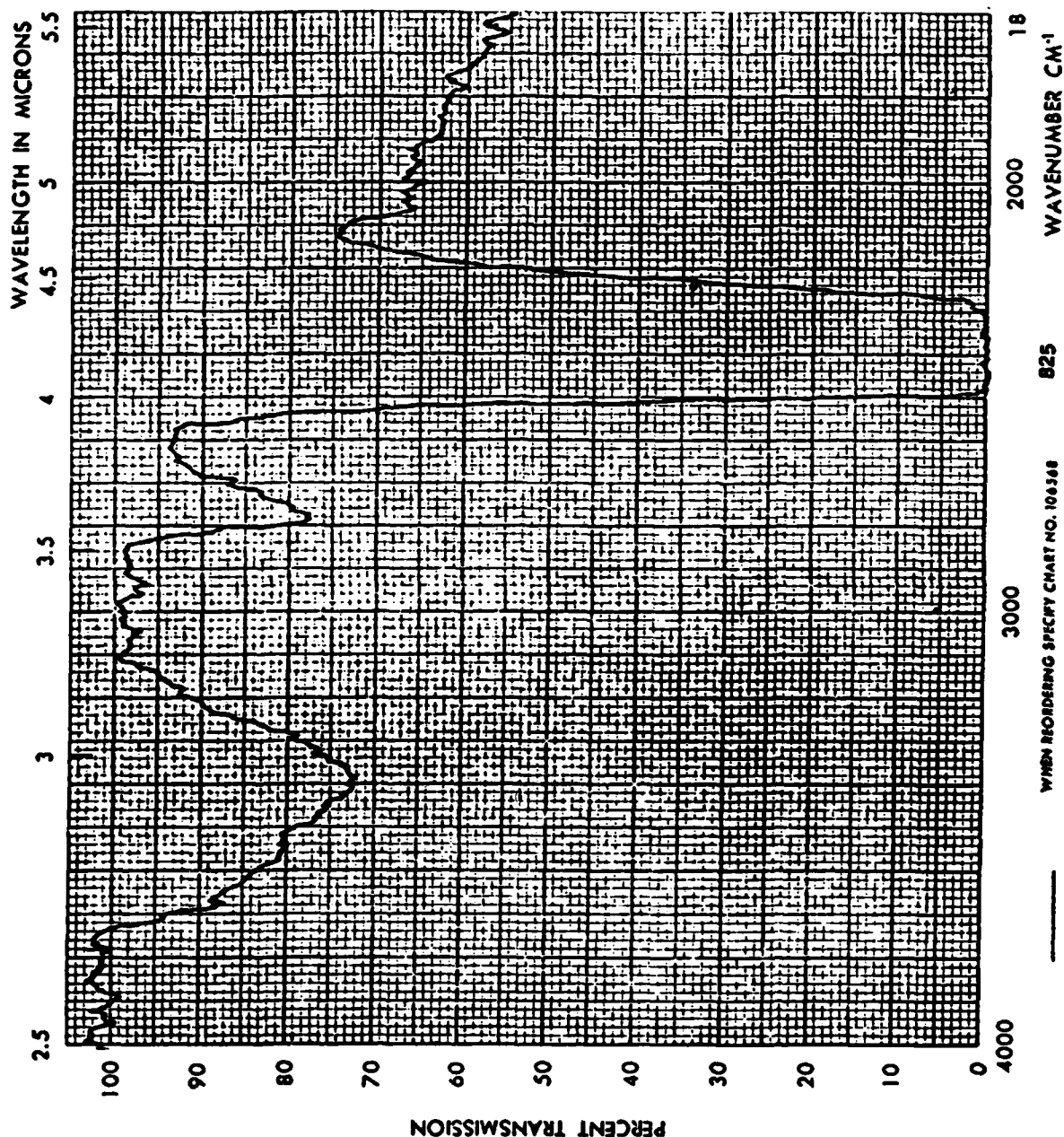


FIGURE 47 - Batch 4 Electrolyte After Reflux

9.4 Cell Balance

Exclusive of tab and grid, each active cell contained 6.7g of calcium. Using a figure of 80A-min/g Ca, this yields 537 A-min, or 8.95 A-Hr. Each cell was vacuum activated with an average of 53 ml of 0.8M $\text{Ca}(\text{AlCl}_4)/\text{SOCl}_2$ electrolyte. This yields a figure of 44.7g SOCl_2 /cell. Using a figure of 27A-min/g for SOCl_2 , this amount of SOCl_2 yields 1208 A-min or 20.1 A-Hr.

The cathodes for the cell, at 1" x 1.25" x .028" nominal, with 20 cathodes, yielded 11.6 cm³ of cathode material. Using the best cathode figures obtained from glass test cells, 0.75 AH/cm³, utilization of this would yield a predicted cathode life of 523 A-min, or 8.7 AH. Since full cells seldom generate utilization as great as that obtained in glass test cells, this figure indicated the cells would be distinctly cathode limited.

9.5 Active Cell Discharge Scheme

Discharge of the cells was accomplished using power supplies, driving the cells at either 80 ma, 400 ma, or 800 ma. Table 45, below, shows the discharge temperatures used and the number of cells discharged under each set of conditions.

TABLE 45 - ACTIVE CELL DISCHARGE SCHEME

Temperatures		Number of Cells		
OC	°F	80 ma Rate	400 ma Rate	800 ma Rate
-54	-65	3	3	-
-29	-20	3	3	-
-18	0	3	3	2
0	+32	3	3	2
+24	+75	3	3	2
+49	+120	3	3	2
+74	+165	3	3	-

9.6 Active Cell Discharge Results

Each cell was vacuum activated with electrolyte, then the fill tube stub was welded shut. After an overnight temperature soak at the indicated environmental temperature, discharge was started. Tables 46, 47 and 48 give discharge data for the cells. The cells designated Nos. 43-48 developed sufficient internal cell pressure to activate 150-psi vents during the stabilization period. From OCV monitoring data taken during the stabilization period, the cells vented from 5-10 hours after being placed in the +74°C oven.

Cells 51-53, discharged at a 400 ma rate at +24°C were prepared identically to cells 18-20. However, instead of being activated one day and discharged the next, cells 51-53 were allowed to stand on ocv for 4 days after activation before being discharged. A-H life for the two sets of cells indicate corrosive attack on the calcium by the electrolyte, as evidenced by the almost 1.5 AH less life achieved by the 4-day old cells.

Discharge curves for the active cells are given as Appendix C to this report.

Post-mortem data on the cells indicated that, as predicted, the cells were cathode limited. All cells, except those venting at +74°C, still contained liquid electrolyte and some calcium. However, it appeared that the calcium was nearly depleted, as what calcium remained was mainly a loose mush, mainly embedded in the separation with some sludge at the cell bottom. None remained as solid material embedded with grid. Some degree of cathode swelling was evidenced by a small amount of rounding of all the can walls parallel to the faces of the cell stack.

TABLE 46 - ACTIVE CELLS PROOF-OF-CONCEPT DISCHARGE

CELL NO.	DISCHARGE RATE, ma	1-20	HOURS TO 2.0V CUTOFF	A-H DISCHARGE LIFE
		ENVIRONMENTAL TEMPERATURE		
1	80	-54°C	0.425	0.034
2	80	-54°C	1.25	0.10
3	80	-54°C	0.90	0.072
4	400	-54°C	2.20	0.88
5	400	-54°C	2.20	0.88
6	400	-54°C	2.15	0.86
7	80	-18°C	60.8	4.86
8	80	-18°C	60.6	4.85
9	80	-18°C	54.9	4.40
10	400	-18°C	9.9	3.96
11	400	-18°C	12.6	5.04
12	400	-18°C	12.4	4.96
13	800	-18°C	5	4
14	800	-18°C	4.94	3.95
15	80	+24°C	68.3	5.46
16	80	+24°C	63	5.04
17	80	+24°C	66	5.28
18	400	+24°C	12.6	5.04
19	400	+24°C	12.55	5.02
20	400	+24°C	13.3	5.32

TABLE 47 - ACTIVE CELLS DISCHARGE DATA SUMMARY
21-39

<u>Cell No.</u>	<u>Discharge Rate, Ma</u>	<u>Environmental Temperature</u>	<u>Hours to 2.0V Cutoff</u>	<u>A-H Discharge Life</u>
21	80	-29°C	52.7	4.22
22	80	-29°C	54	4.32
23	80	-29°C	56	4.48
24	400	-29°C	8.8	3.52
25	400	-29°C	9	3.6
26	400	-29°C	10.9	4.35
27	80	0 °C	69.5	5.56
28	80	0°C	70.5	5.64
29	80	0°C	70.1	5.61
30	400	0°C	11.5	4.6
31	400	0°C	12.97	5.2
32	400	0°C	13.1	5.24
33	800	0°	5.84	4.67
34	800	0°C	5.83	4.66
35	800	+49°C	3.12	2.5
36	800	+49°C	3.38	2.7
37	400	+49°C	9.65	3.86
38	400	+49°C	9.65	3.86
39	400	+49°C	9.52	3.81

TABLE 48 - ACTIVE CELLS DISCHARGE DATA SUMMARY
40-53

<u>Cell No.</u>	<u>Discharge Rate, Ma</u>	<u>Environmental Temperature</u>	<u>Hours to 2.0V Cutoff</u>	<u>A-H Discharge Life</u>
40	80	+49°C	39.8	3.18
41	80	+49°C	39.6	3.17
42	80	+49°C	39.46	3.15
43	80	+49°C	39.46	3.15
44				
45				
46	+74°C - all vented during overnight heat			
47	soak prior to discharge			
48				
49	800	+24°C	4.66	3.73
50	800	+24°C	4.71	3.77
51	400	+24°C	9.14	3.66
52	400	+24°C	9.35	3.74
53	400	+24°C	9.16	3.66

SECTION X

SECOND PHASE - RESERVE CELL WORK

10.1 Electrolyte Comparison

Commercially prepared 3:1 electrolyte (3 Molar AlCl_3 :1 Molar LiCl) / SOCl_2 from Lithium Corporation of American was purchased for comparison purposes with the Eagle-Picher prepared electrolyte. Bag cells and IR scan were used to compare the electrolytes.

Bag cells prepared using one cathode, dry pressed 1" x 1.875" x 100" composed of 8% TFE binder and 92% Carbon Black sandwiched between two Calcium .010" thick anodes slightly larger than the cathode. Dexter 255 separator was folded once around the cathode. Approximately 15 ml of electrolyte was used to activate each cell. A constant resistive load of 4.3 ohm was used to discharge each cell to a 2.0 cut-off voltage (see chart below). Lab prepared 3:1 electrolyte used Fluka AlCl_3 and LiCl and Kodak SOCl_2 .

3: 1 Lab Electrolyte Versus 3:1 Lithcoa Electrolyte

<u>Electrolyte</u>	<u>Load (Ohms)</u>	<u>OCV</u>	<u>Discharge Range</u>	<u>Discharge Minutes</u>
Lab	4.3	3.28	2.53-2.0	29
Lab	4.3	3.39	2.80-2.0	20
Lab	4.3	3.36	2.68-2.0	30
Lithcoa	4.3	3.34	2.70-2.0	31

I.R. scans of the Lab prepared electrolyte and Lithcoa electrolyte were obtained on a Beckman AccuLab II Spectrophotometer using a KBr wet cell having 0.1 mm path. The scans were evaluated for the presence of contaminants only and not for relative amounts. (See Figures 48 and 49 for data).

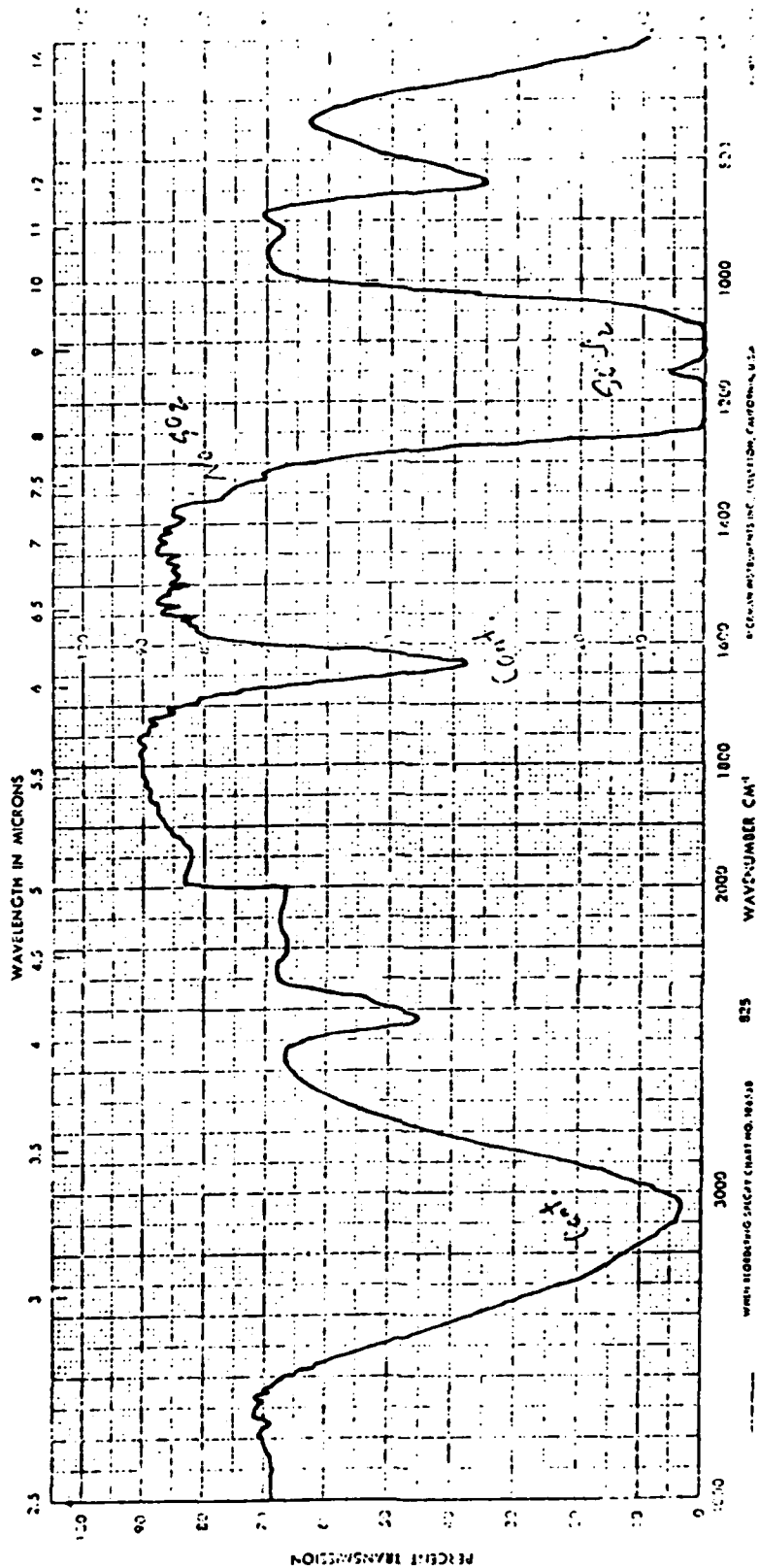


FIGURE 48 - IR Scan - Lithcoa 3:1 Electrolyte

190
4/5/84
3:1 Electrolyte
Lithcoa

0.1
Concentration
Liquid
For Ref
GT

Wavenumber

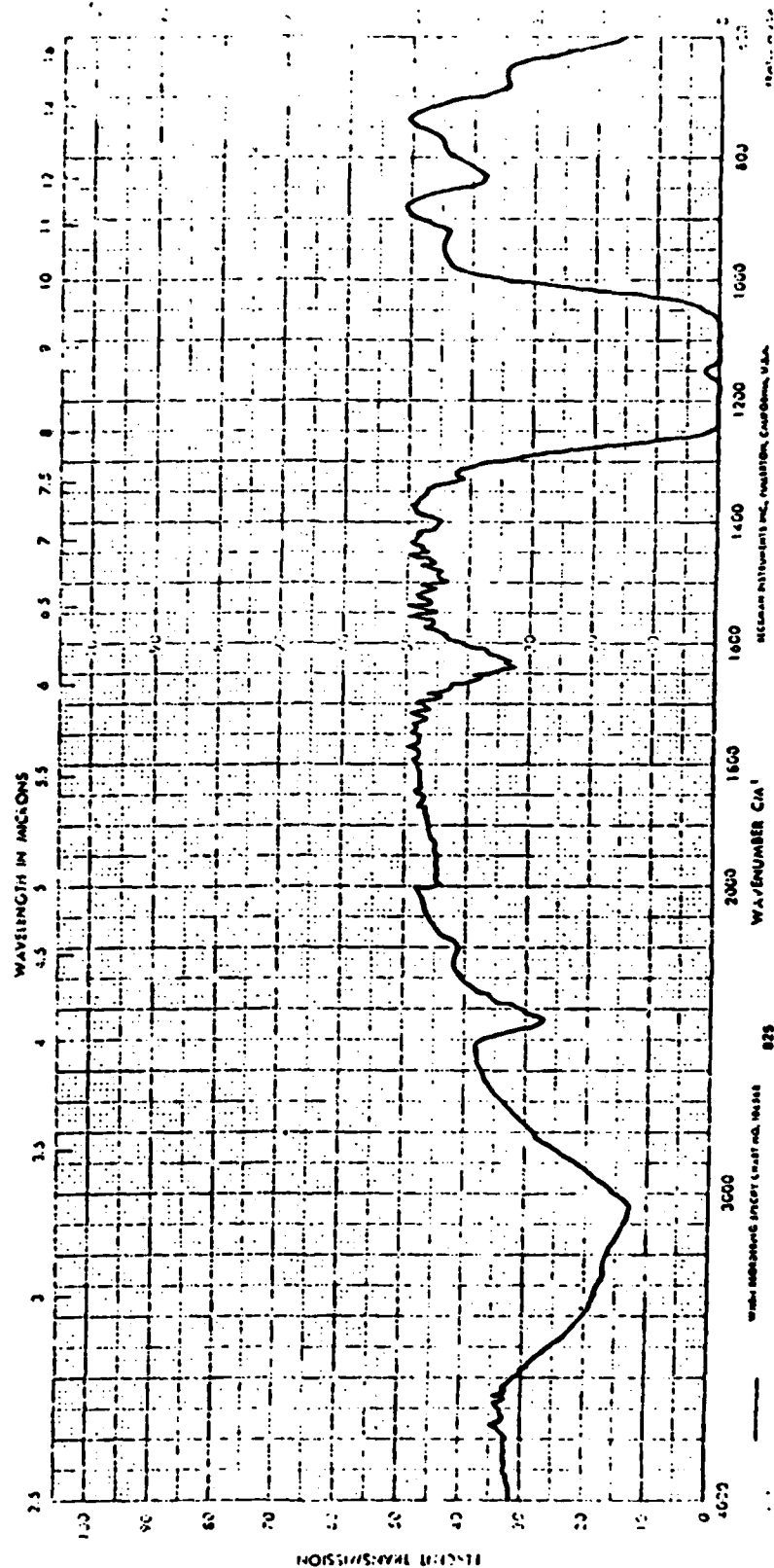


FIGURE 49 - IR Scan - E-P 3:1 Electrolyte

172
3/2/54
Electrolyte
Electrolyte
Electrolyte
Electrolyte
Electrolyte

Electrolyte
Electrolyte
Electrolyte
Electrolyte
Electrolyte
Electrolyte
Electrolyte

Electrolyte

The Lithcoa prepared 3:1 electrolyte did not appear to be of significantly better quality or give better bag cell performance than Lab prepared electrolyte.

10.2 Electrolyte Full Cell Comparison

A matrix of stainless steel rectangular D-cells was constructed. Cathodes utilized were one of two types. Cells 1-5 were prepared using cathodes of 10% TFE content, pressed in the usual manner. Cells 6-8 used cathodes of 2% TFE content, pressed and then sintered at 550°F. The purpose of the cathode difference was to determine if the handling properties of the cathodes could be improved without a large loss of performance. Part of the cells were activated with Lithcoa Company commercially-prepared 3:1 (3M AlCl_3 :1M LiCl) electrolyte. The rest were activated with Eagle-Picher prepared electrolyte of either 3:1 or 2:2/3 AlCl_3 : LiCl concentrations. The purpose of the electrolyte differences was to compare performance of the Lithcoa electrolyte to that prepared by Eagle-Picher, and to determine if the gassing reaction between the anode and electrolyte could be lessened by use of a more balanced electrolyte (the 2:2/3). Technical data and discharge results for the cells are given in Table 49, and voltage and temperature curves are given as Figures 50-57.

As may be seen from the data in Table 49, the cells activated with the Eagle-Picher prepared electrolyte performed slightly better than those activated with the Lithcoa electrolyte. The cells activated with 2:2/3 electrolyte performed comparably or better than those activated with either of the other electrolytes. Cell 8, which had 2% TFE sintered cathodes, equalled the performance of the best cell containing cathodes with 10% TFE content, indicating that the sintered cathodes may not impose a performance penalty.

Only one of the cells, Number 3, activated with Lithcoa 3:1 electrolyte, vented through the cell cover vent sticker. However, since the fill tubes were only crimped after activation, it is likely that only cell Number 3 had a sufficiently hermetic seal to allow significant gas pressure buildup.

TABLE 49- TECHNICAL DATA FOR FIGURES 50-57

Figure	50	51	52	53	54	55	56	57
V	2.09	2.11	2.13	2.05	2.09	2.20	2.10	2.09
VH	0.63	0.87	0.67	0.80	0.80	0.70	0.52	0.91
AH	1.25	1.70	1.35	1.58	1.53	1.50	1.10	1.70
AH/Cm ³	0.04	0.06	0.05	0.05	0.05	0.05	0.04	0.06
Mix	10% UB	10% UB	10% UB	10% UB	10% UB	2% Bak	2% Bak	2% Bak
Thickness	0.120"	0.120"	0.120"	0.120"	0.120"	0.120"	0.120"	0.120"
Quality	8	8	8	8	8	8	8	8
Electrolyte	Lithcoa 3:1	Lab 3:1	Lithcoa 3:1	Lab 2:2/3	Lab 3:1	Lab 3:1	Lab 3:1	Lab 2:2/3
Ohms Load	0.5	0.5	0.5	0.5	0.5	0.47	0.48	0.53
Temp.Max	100C	130C	120C	100C	120C	120C	90C	90C

Note: All cells constructed with 8 cathodes, 1" x 1.875" x .120", activated with 40 ml electrolyte, 9 Ca anodes, .010" thick, with .010" Dexter 255 separation.

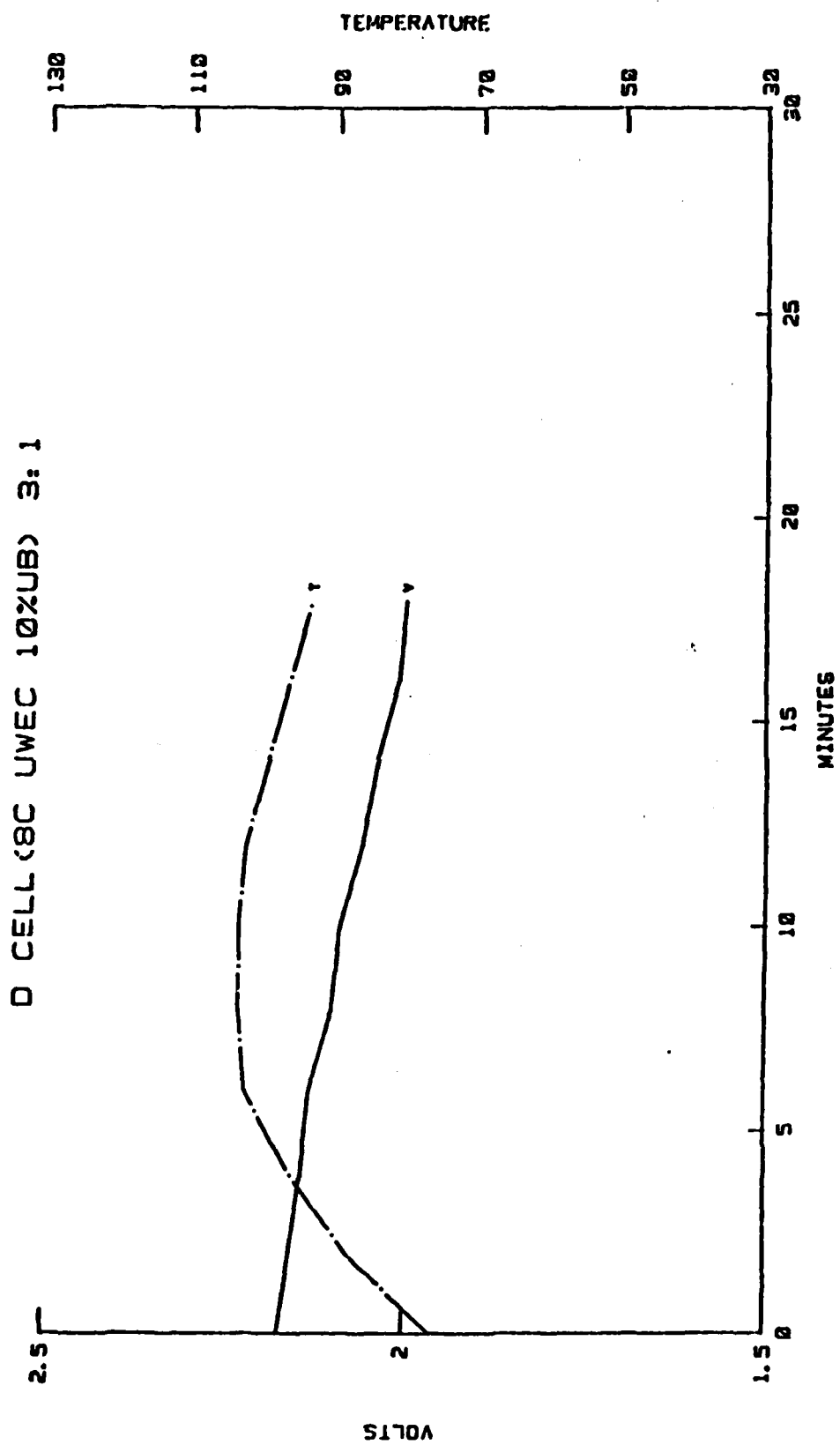


FIGURE 50 D-Cell Discharge No. 1

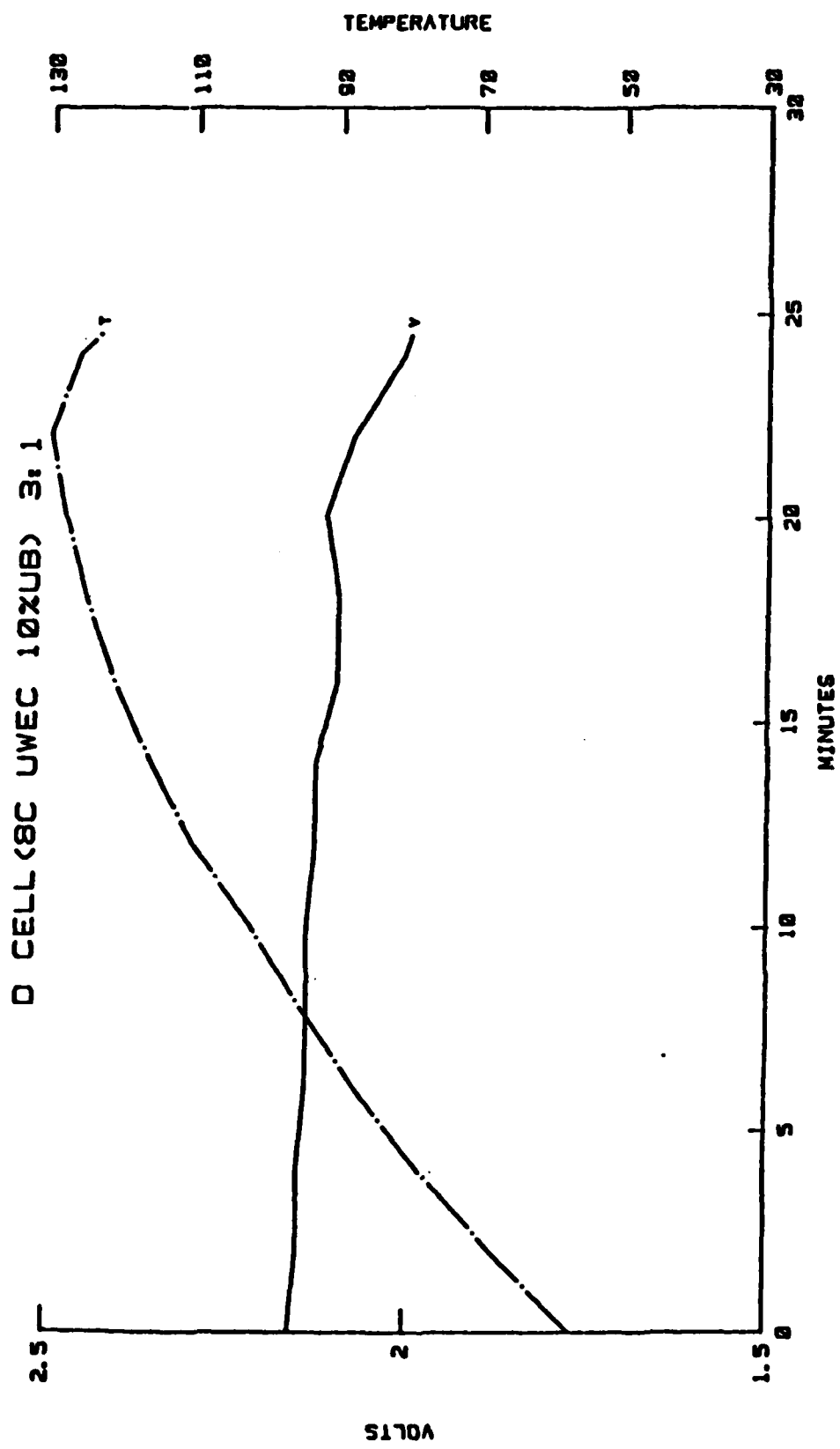


FIGURE 51 D-Cell Discharge No. 2

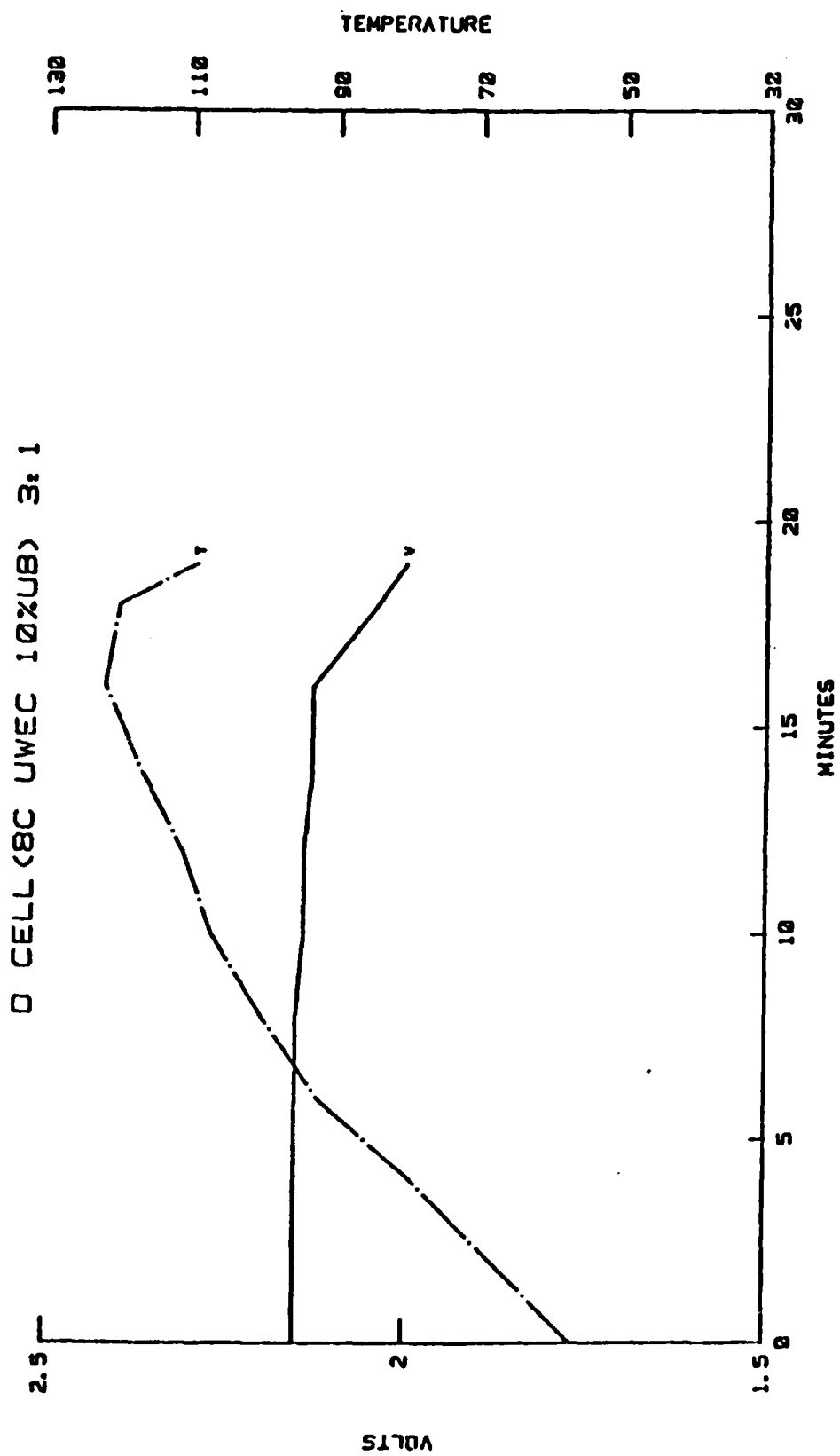


FIGURE 52 D-Cell Discharge No. 3

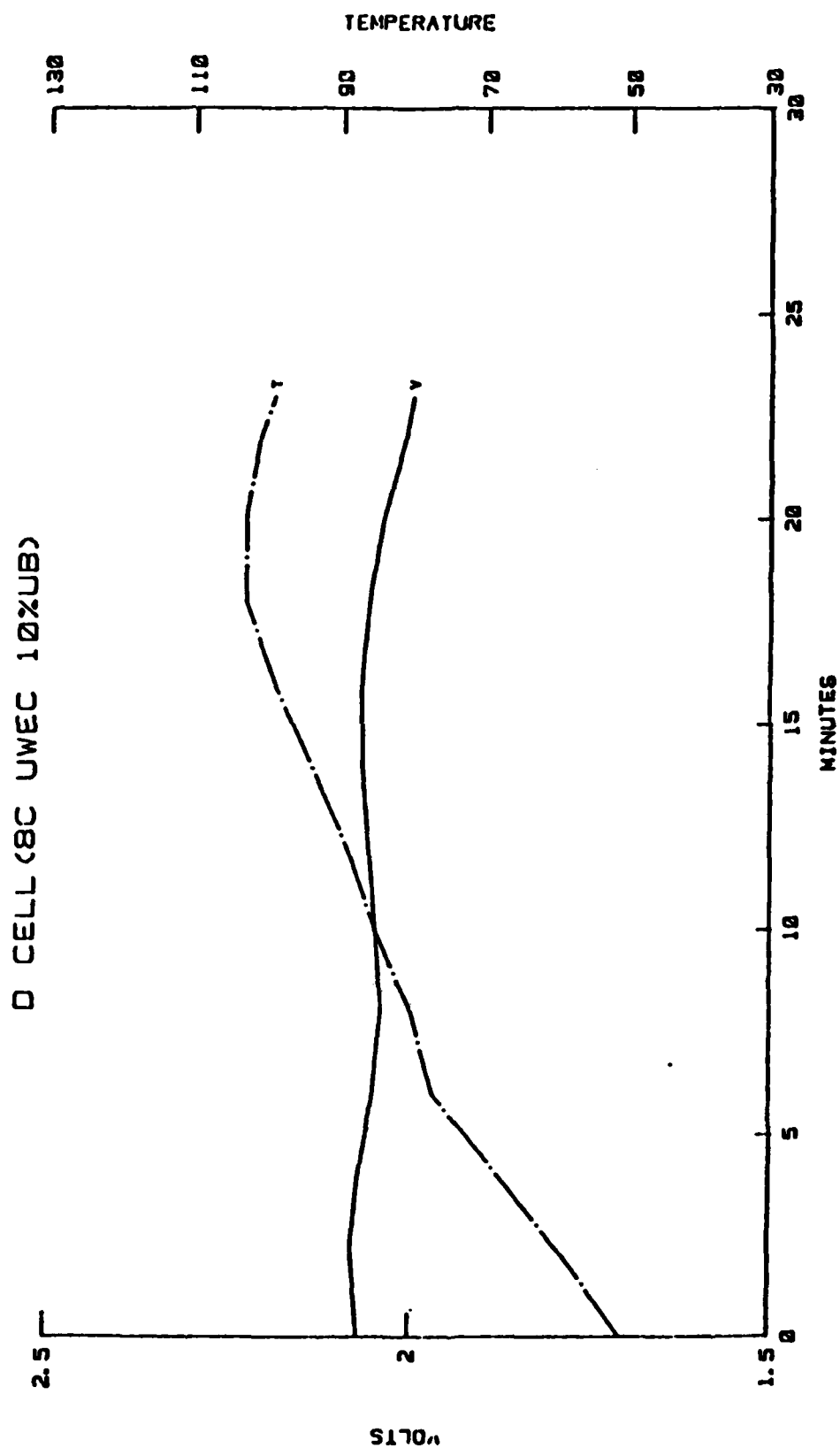


FIGURE 53 D-Cell Discharge No. 4

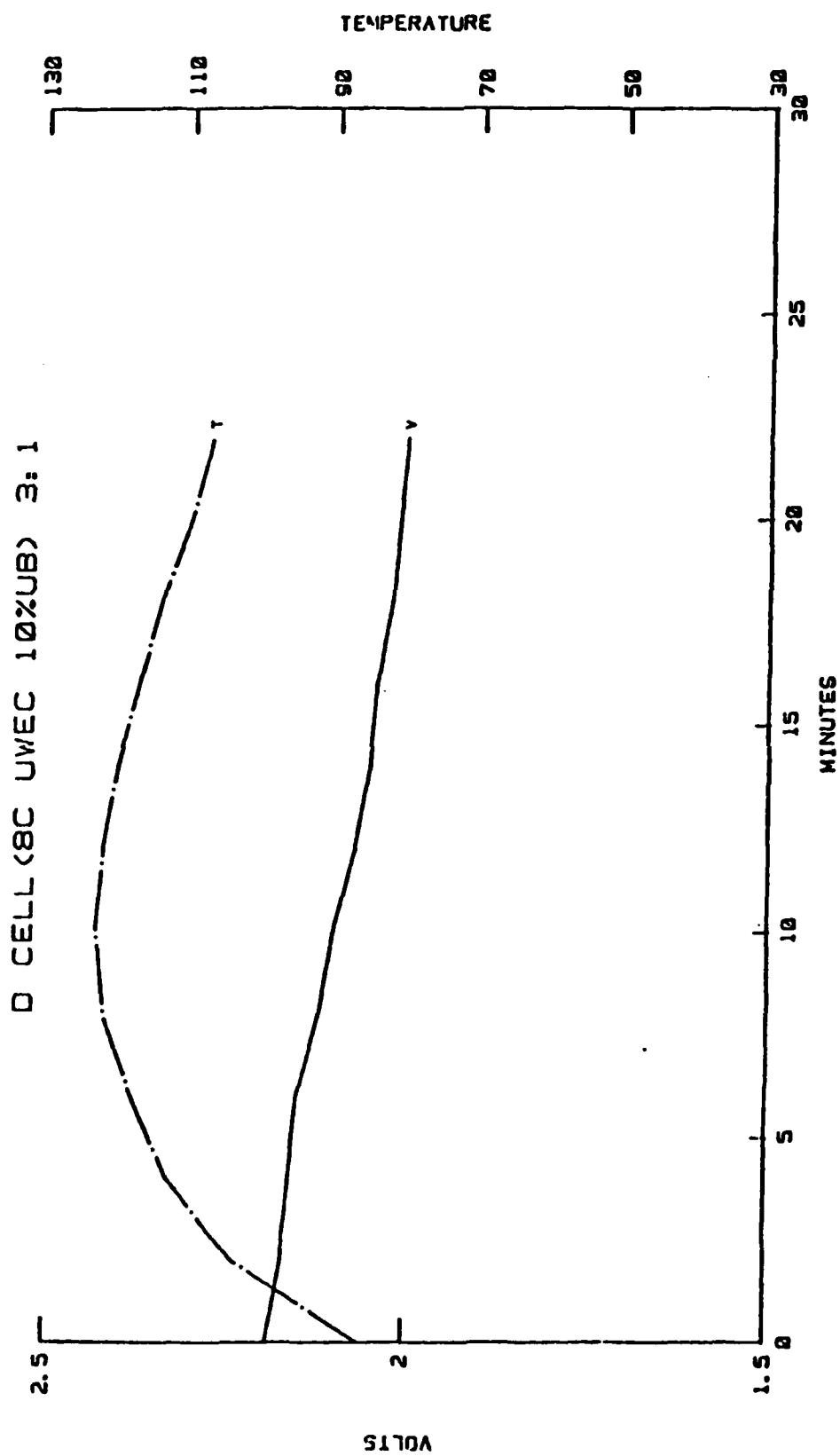


FIGURE 54 D-Cell Discharge No. 5

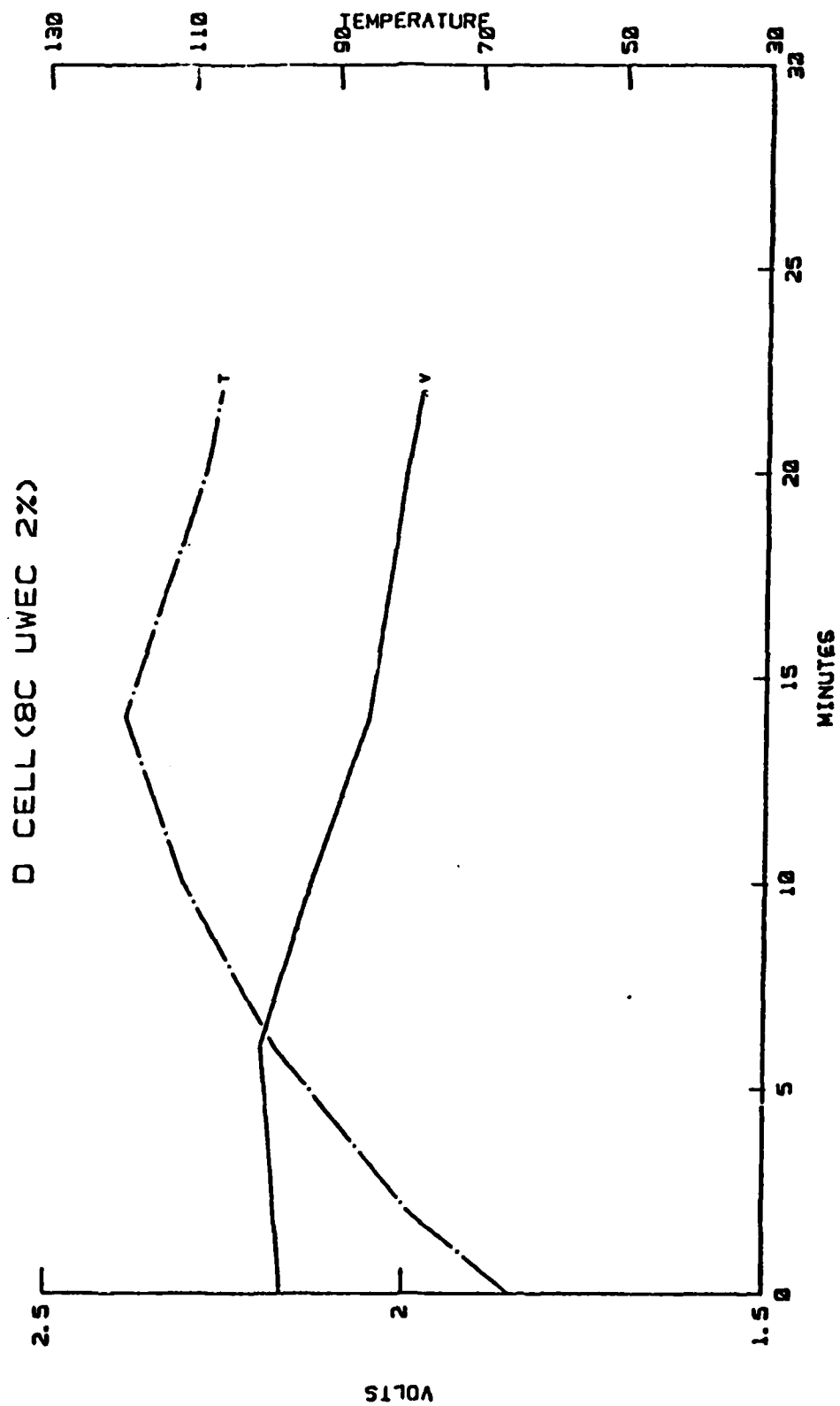


FIGURE 55 D-Cell Discharge No. 6

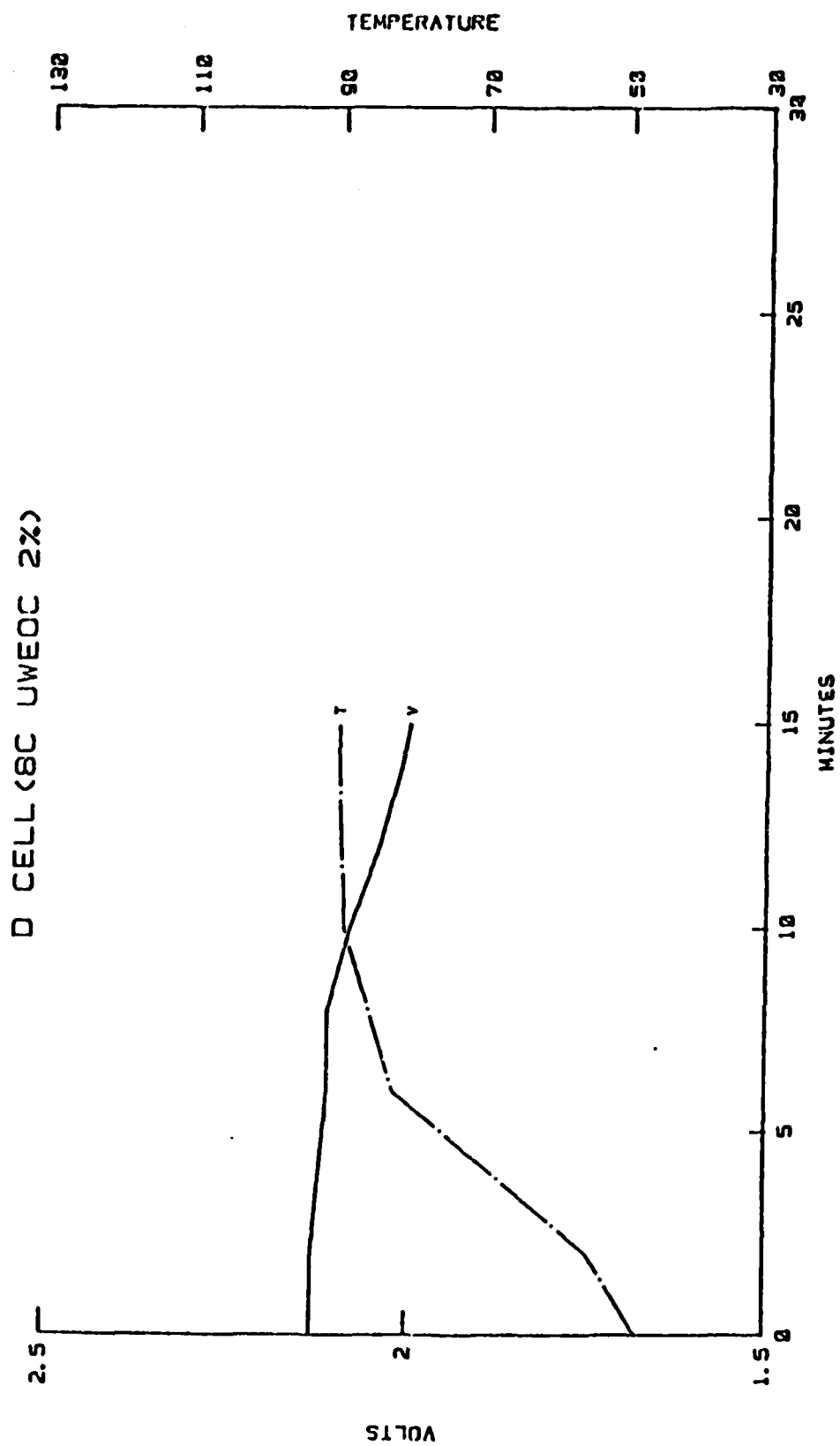


FIGURE 56 D-Cell Discharge No. 7

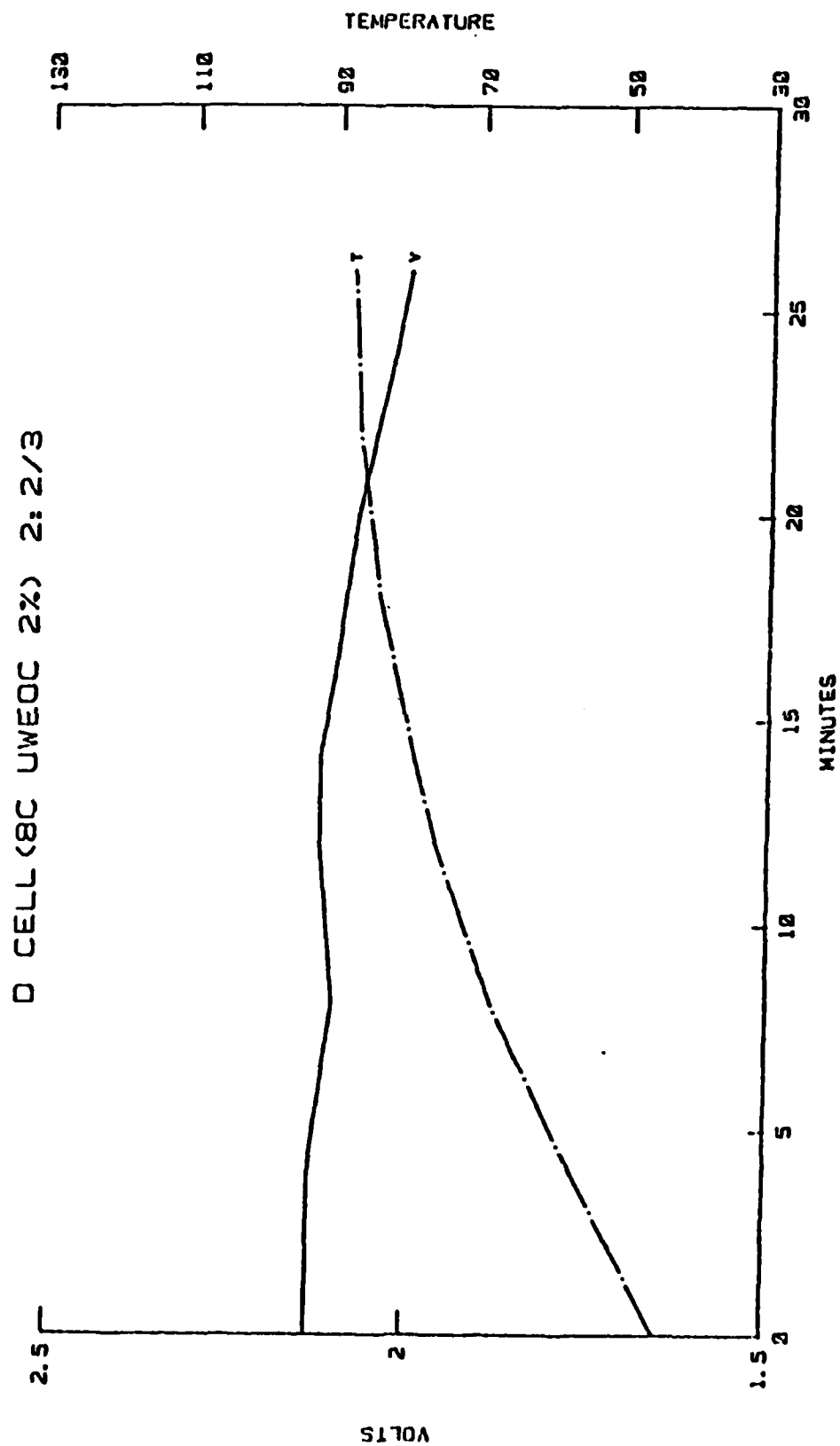


FIGURE 57 D-Cell Discharge No. 8

10.3 Copper Additive Cathode Discharges

Four rectangular, stainless steel D-cells were constructed identically to the cell series described in the preceeding section of this report, with the exception that the cathodes utilized contained one of two additives, copper phthalocyanine or copper dust. The cathodes had either 15% Cu Phth, 15% Cu dust, or 50% Cu dust added to the cathode 2% TFE dry mix. Cathodes were then pressed and finally sintered at 620°F for 20 minutes. Technical details on cell composition and discharge data for the cells are given in Table 50. Discharge curves for the cells are given as Figures 58-60. The D-cell containing the 50% Cu dust cathodes could not be activated due to immediate and vigorous reaction with the 3:1 electrolyte employed.

Comparison of the results of these cells with cells 53 and 54 from Table 49 indicate that neither of the additives improved cell performance. The varying ohm load indicated for the cell containing the 15% Cu dust cathode additive was necessitated by the cell's initial inability to maintain voltage above 2.0 under the 0.4 ohm load utilized with the other cells. As the discharge proceeded it was found that the cell could handle increased load, and was slowly loaded to the 0.48 ohm level.

The two cells with cathodes containing copper phthalocyanine at the 15% level achieved fewer amp-hours above 2.0 volts than the corresponding cells without the additive, nor were temperatures reached significantly less. Cell 9 shows a steady temperature at 110°C. However, this cell began venting at 3 minutes into the discharge. Cell 57, with the same composition, was discharged with the vent sticker disabled, and showed a steady temperature rise until at a little over 10 minutes into the discharge the cell failed mechanically.

TABLE 50 - TECHNICAL DATA FOR FIGURES 58-60

<u>FIGURE</u>	<u>58</u>	<u>59</u>	<u>60</u>
\bar{V}	2.09	2.08	2.08
VH	0.38	0.38	0.76
AH	0.95	0.95	1.09
AH/Cm ³	0.04	0.04	0.04
Mix	2% Bak-15% Cu Phth	2% Bak-15% Cu Phth	2% Bak-15% Cu
Thickness	0.100"	0.100"	0.100"
Quantity	8	8	8
Electrolyte	Lab 3:1	Lab 3:1	Lithcoa 1.5M
Ohms Load	0.4	0.4	1.35-0.48
Temp. Max	110C	130C	100C

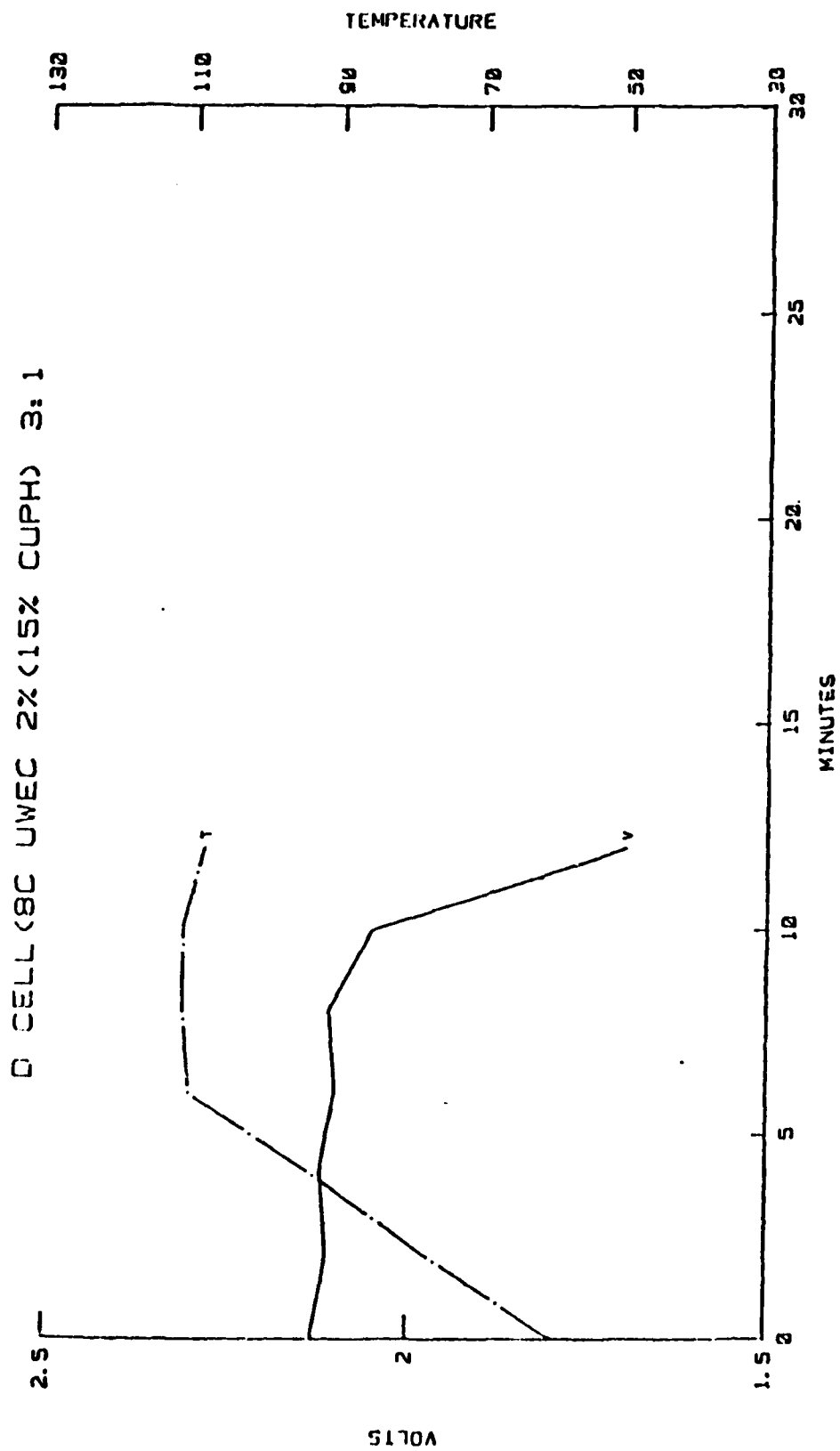


FIGURE 58 D-Cell Discharge No. 9

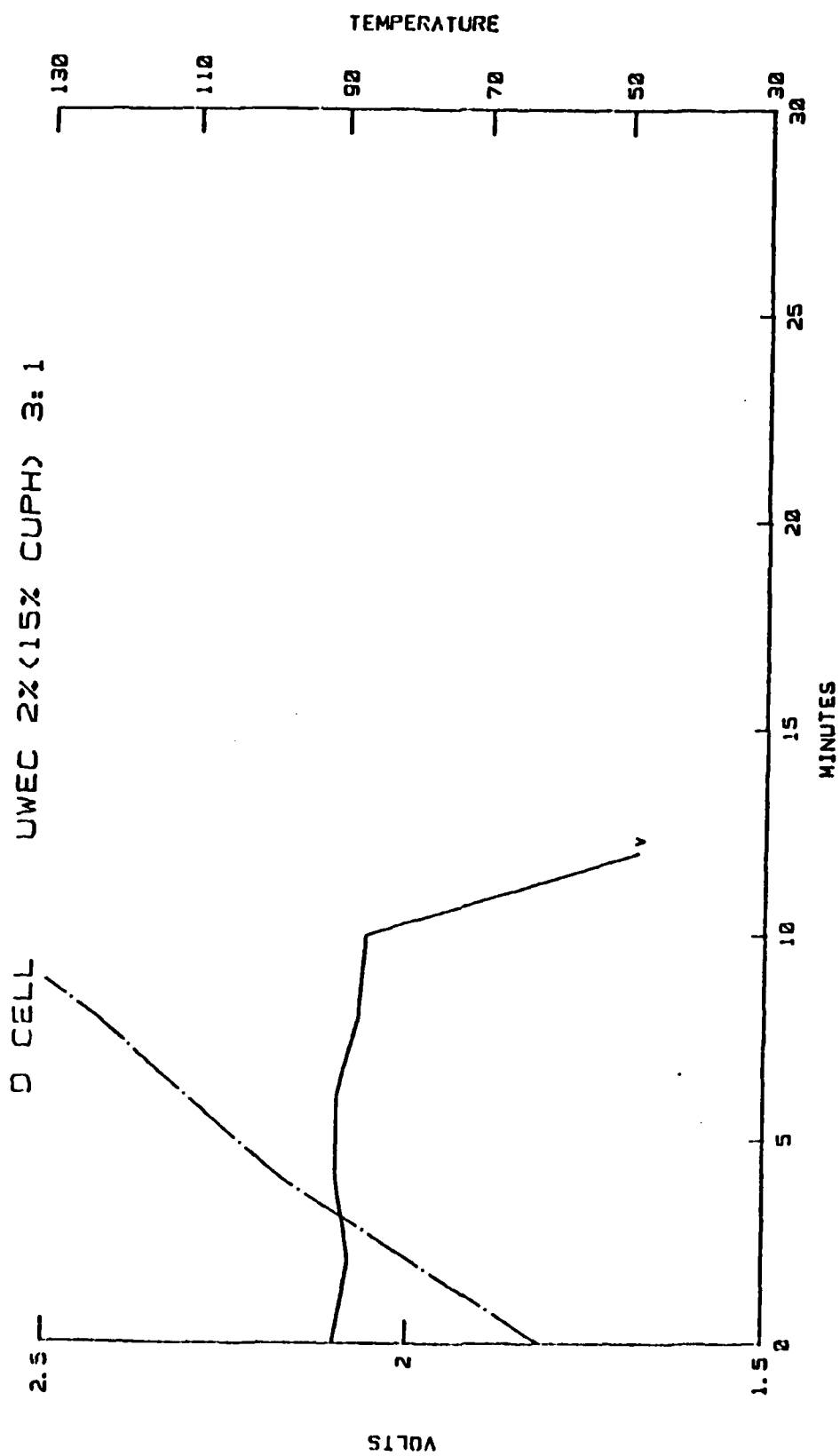


FIGURE 59 D-Cell Discharge No. 10

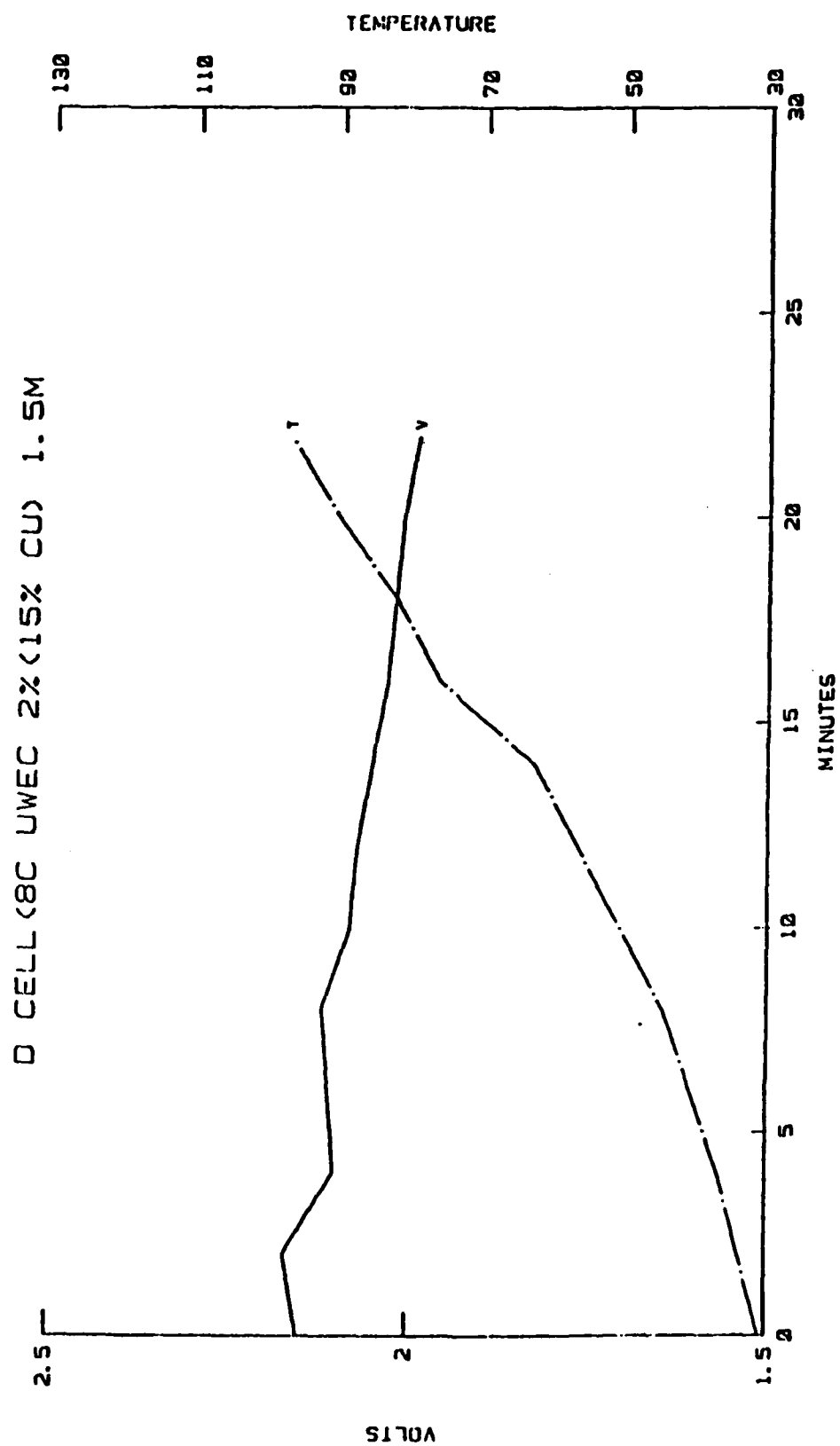


FIGURE 60 D-Cell Discharge No. 11

SECTION XI
THIRD PHASE RESERVE CELL WORK

11.1 Carbon Substitute Investigation

A preliminary evaluation was made of two potential substitutes for the Sawinigan 50% compressed carbon utilized for all the preceeding cathodes. Two activated charcoals, one from Fisher Scientific, the other from the Barnaby-Cheney Co., were utilized. The charcoals were ground in mortar and pestle, wet pasted with 10% TFE binder, allowed to dry for 48 hours, sintered at 620°F for 20 minutes, then dry pressed with grid at 2000 psi. Integrity of the cathodes was poor. Pressing at pressures above 2000 psi caused warpage and cracking of the cathodes. Several trials of these cathodes against the standard cathode were made in Table 51 below is given performance data of typical runs. Neither of the activated charcoals exceeded the performance of the standard cathode. The Discharge Tests were conducted in bag cells with the cathode, U-wrapped in Dexter separator, sandwiched between two anodes.

TABLE 51 - TYPICAL CHARCOAL PERFORMANCE

	<u>Bag Control Cell</u>	<u>Bag Cell #1</u>	<u>Bag Cell #2</u>
Cathode (1)	Standard	Fisher Carcoal	Barnaby-Cheney
Cathode Size	1"x1.875"x.050"	1"x1.875"x.050"	1"x1.875"x.050"
Anode (2)	.010" Ca	.010" Ca	.010" Ca
Electrolyte 12 ml	Lab 3:1	Lab 3:1	Lab 3:1
OCV	3.28	3.17	3.20
Load (Ohms)	4.5	4.5	4.5
Discharge Time (min.)	26	26	20
Above 2.0V			

11.2 Thinner Cathode Comparison

Thinner cathodes were evaluated in a stainless-steel D-cell as a means to improve cathode utilization (AH/cm³). Cathodes of .050 inch thickness allowed 11 to be stacked on the cell, compared to 8 at .100 inch or 7 at .130 inch. One of the D-cells utilized fluted (corrugated) cathodes, to see if the improved electrolyte flow into the stack and increased surface area would improve performance. Technical data for the cells is given in Table 52. Discharge curves are given in Figures 61 - 64.

The fluted-cathode cell performed poorly compared to the standard cathode cells. The cell with eleven .050 inch cathodes showed a significant increase in performance over the thicker-cathode cells.

TABLE 52 - TECHNICAL DATA FOR FIGURES 61-64

	<u>61</u>	<u>62</u>	<u>63</u>	<u>64</u>
\bar{V}	2.09	2.10	2.07	2.07
Vh	0.42	0.53	0.70	1.00
Ah	0.84	1.05	1.38	2.20
AH/cm ³	0.03	0.04	0.05	0.13
Cathode Mix	5% Baked	10% Unbaked	10% Unbaked	2% Baked
Thickness	0.125"	0.100"	0.120"	0.050"
Quality	8	7	7	11
Electrolyte Lab	2:1	Lab 3:1	Lab 3:1	2:2/3
Ohms Load	0.5	0.5	0.5	0.46
Max. Temp.	-	-	115C	130C

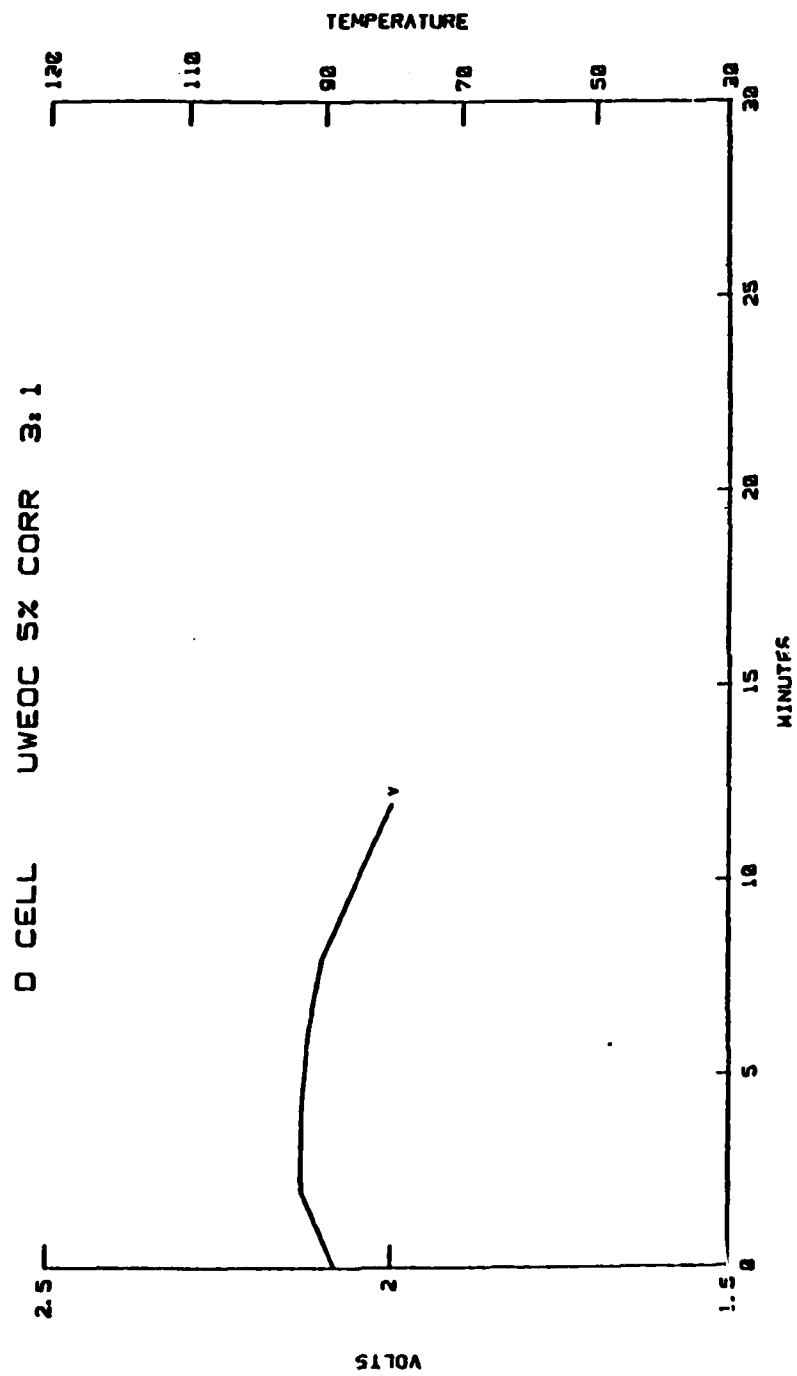


FIGURE 61 D-Cell - 2:1 Electrolyte

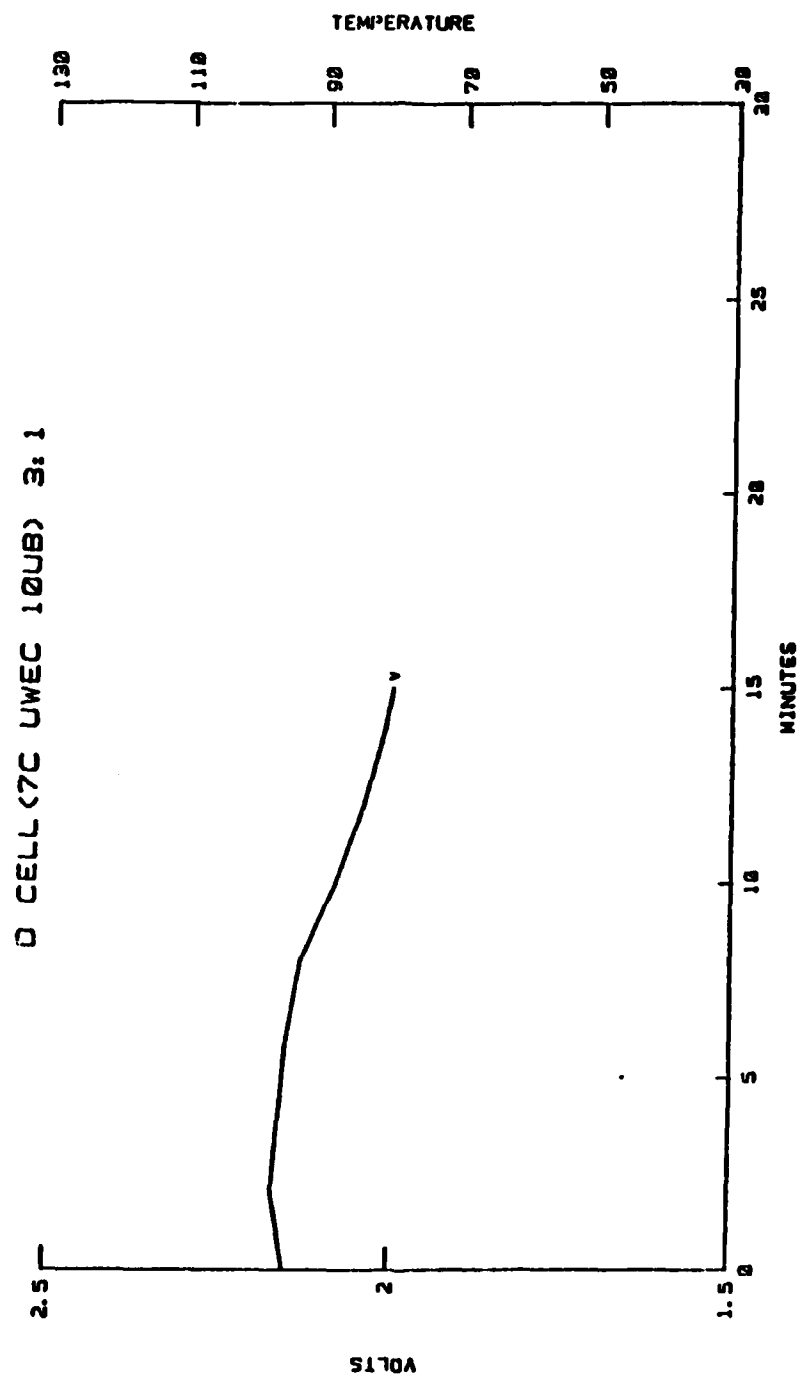


FIGURE 62 D-Cell Lab 3:1 Electrolyte

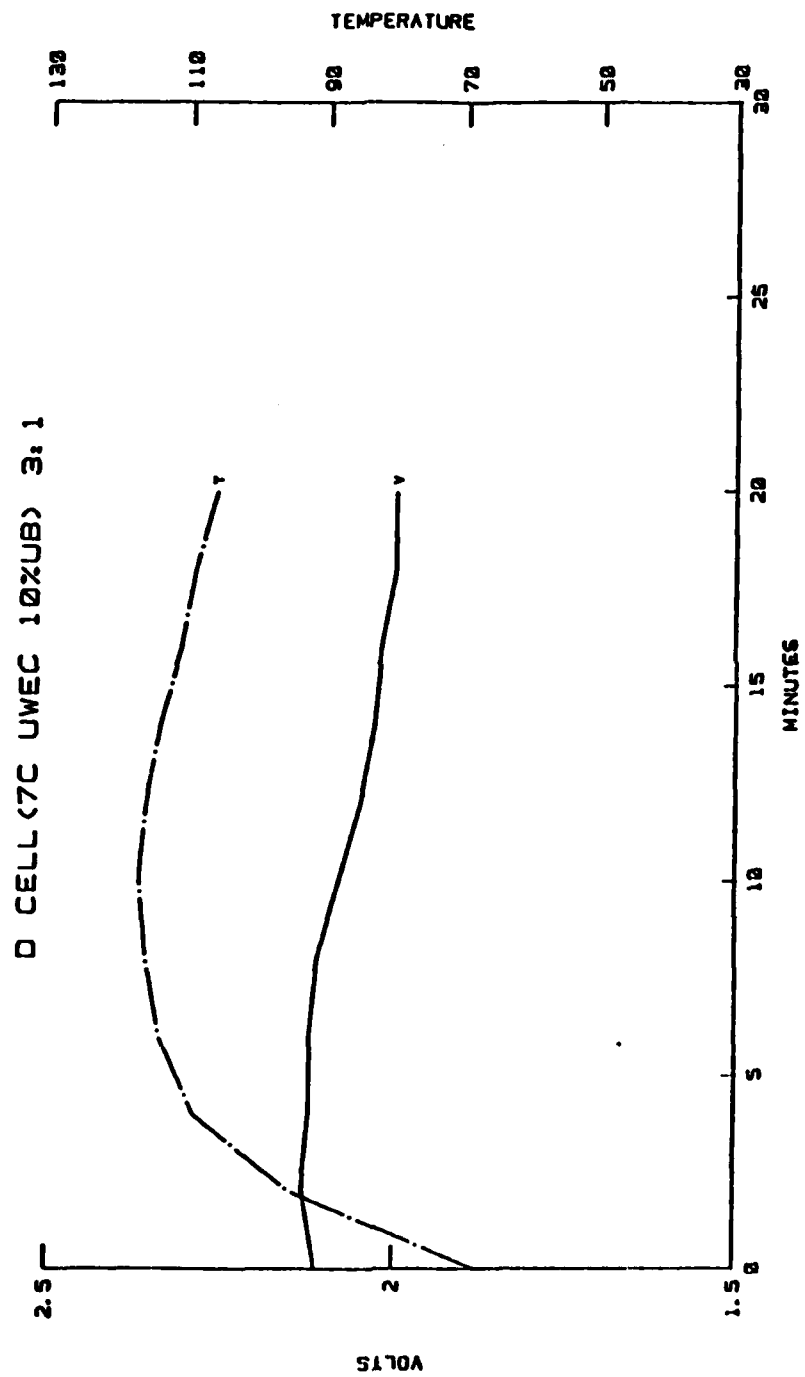


FIGURE 63 D-Cell-Lab 3:1 Electrolyte/Thicker Cathodes

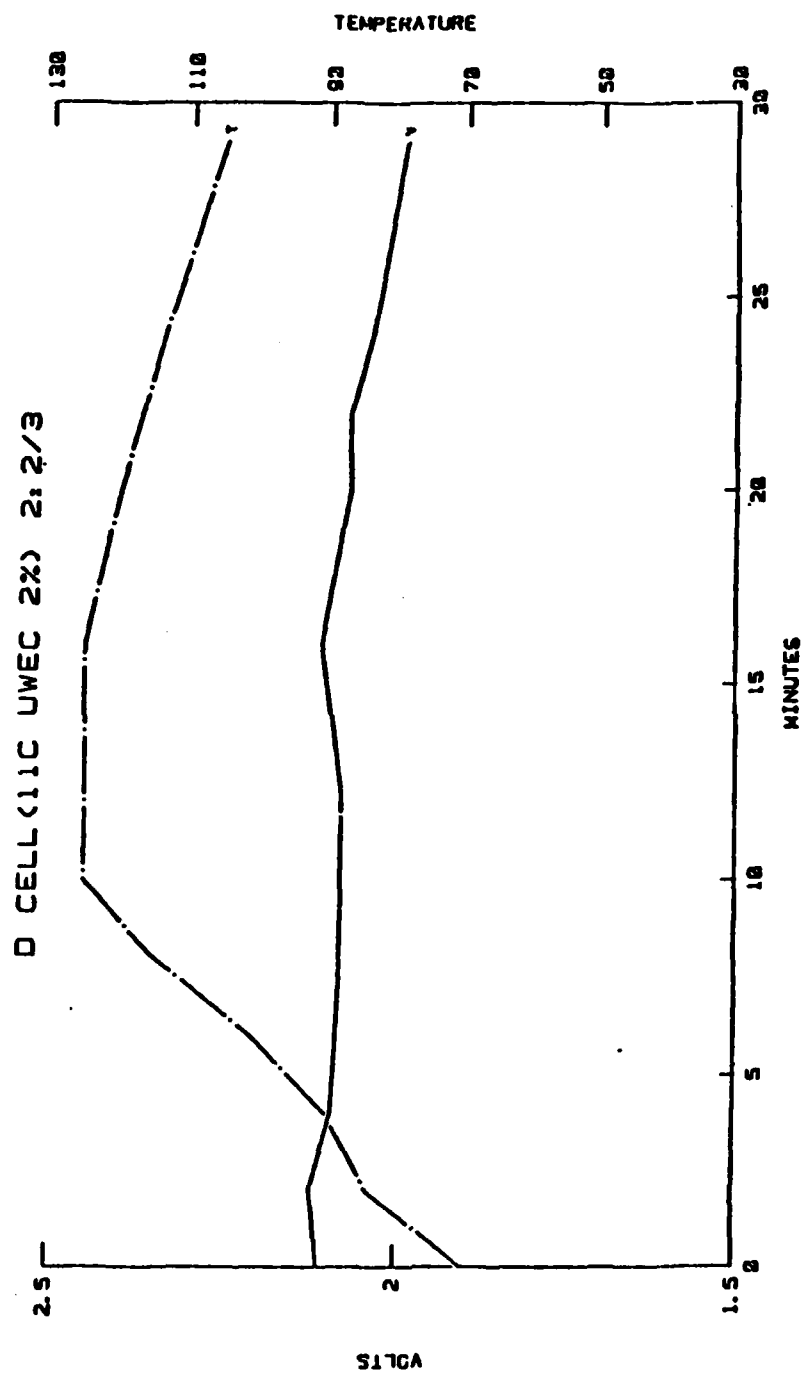


FIGURE 64 D-Cell-Lab 2:2/3 Electrolyte

11.3 Cells Discharges - Thinner Cathodes w/Additives

A series of S.S. hermetically sealed D-cell tests were conducted with 0.050" thick cathodes, copper dust and copper phthalocyanine (Phth.) cathode additives, using 1.5M LiAlCl₄ and 2:2/3 (2MAlCl₃:2/3M LiCl) electrolytes to help reduce cell gassing. All cells contained 15 cathodes, 1" x 1.875" x .050", U-wrap 0.10" thick Ca anodes on every other cathode, U-wrapped in Dexter separator. The standard cathode mix was 2% TFE binder/CB baked for 20 minutes at 620F. Additives were blended into the cathode mix at the following concentrations: Copper Dust 15%, Copper Phth. 10% and 15% levels. Control cells composed of 2% TFE binder/CB with no additives were discharged with each of the two electrolytes, 1.5M LiAlCl₄ and 2:2/3. See Table 53, for control cell discharge data, and Figures 65-67 for discharge curves.

TABLE 53 - TECHNICAL DATA FOR FIGURES 65-67

<u>Figure</u>	<u>65</u>	<u>66</u>	<u>67</u>
<u>V</u>	2.08	2.05	
VHr	0.75	0.90	0.75
AHr	1.62	1.39	1.30
AHr/CM3	0.07	0.06	0.06
Mix	Control	Control	Control
Thickness	0.050"	0.050"	0.050"
Quality	15	15	15
Electrolyte	2:2/3	1.5 LiAlCl ₄	1.5 LiAlCl ₄
Avg. Ohms Load	0.463	0.645	0.577
Temp. Max.	111C	92C	81C

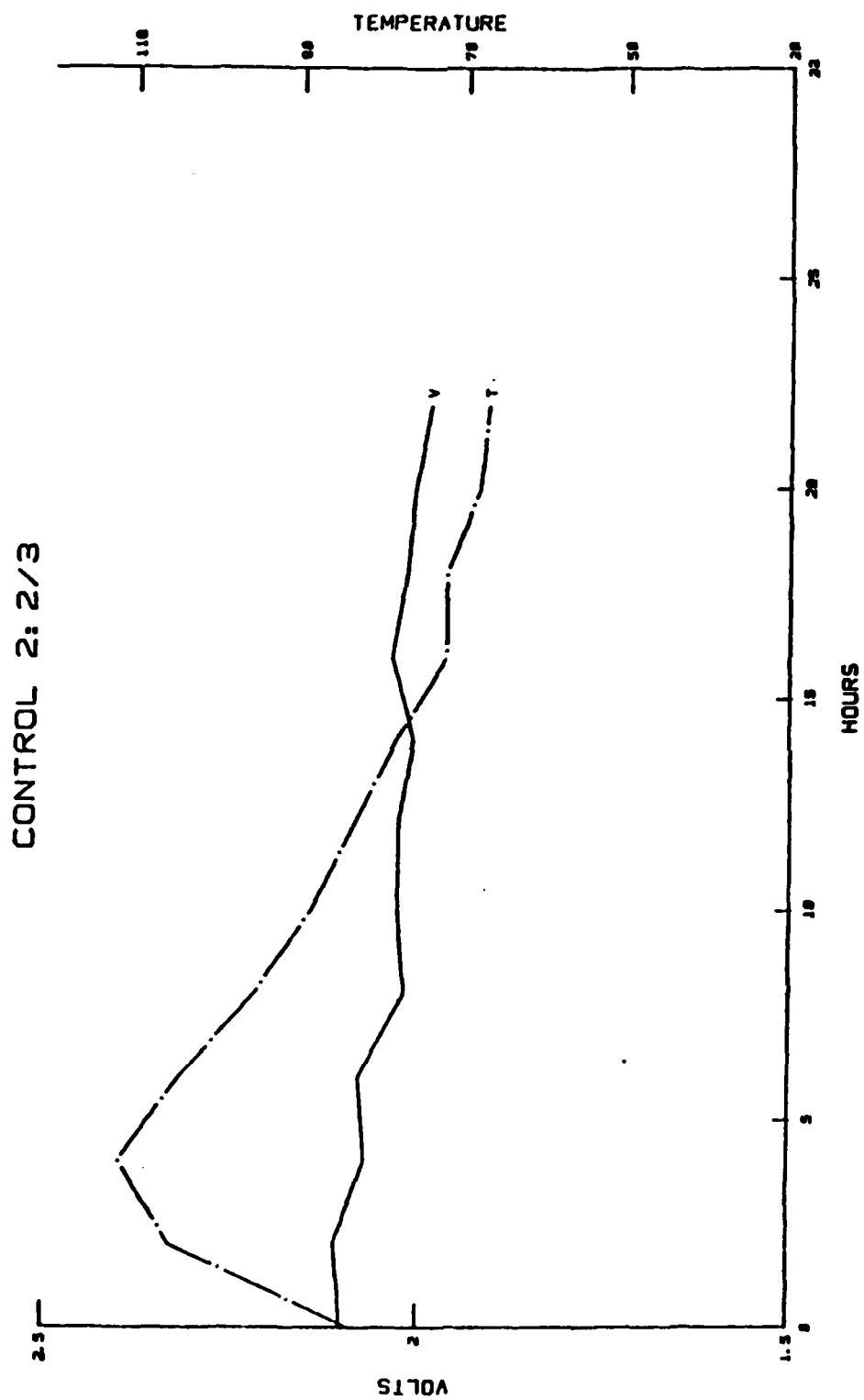


FIGURE 65 Control Cell-2:2/3 Electrolyte

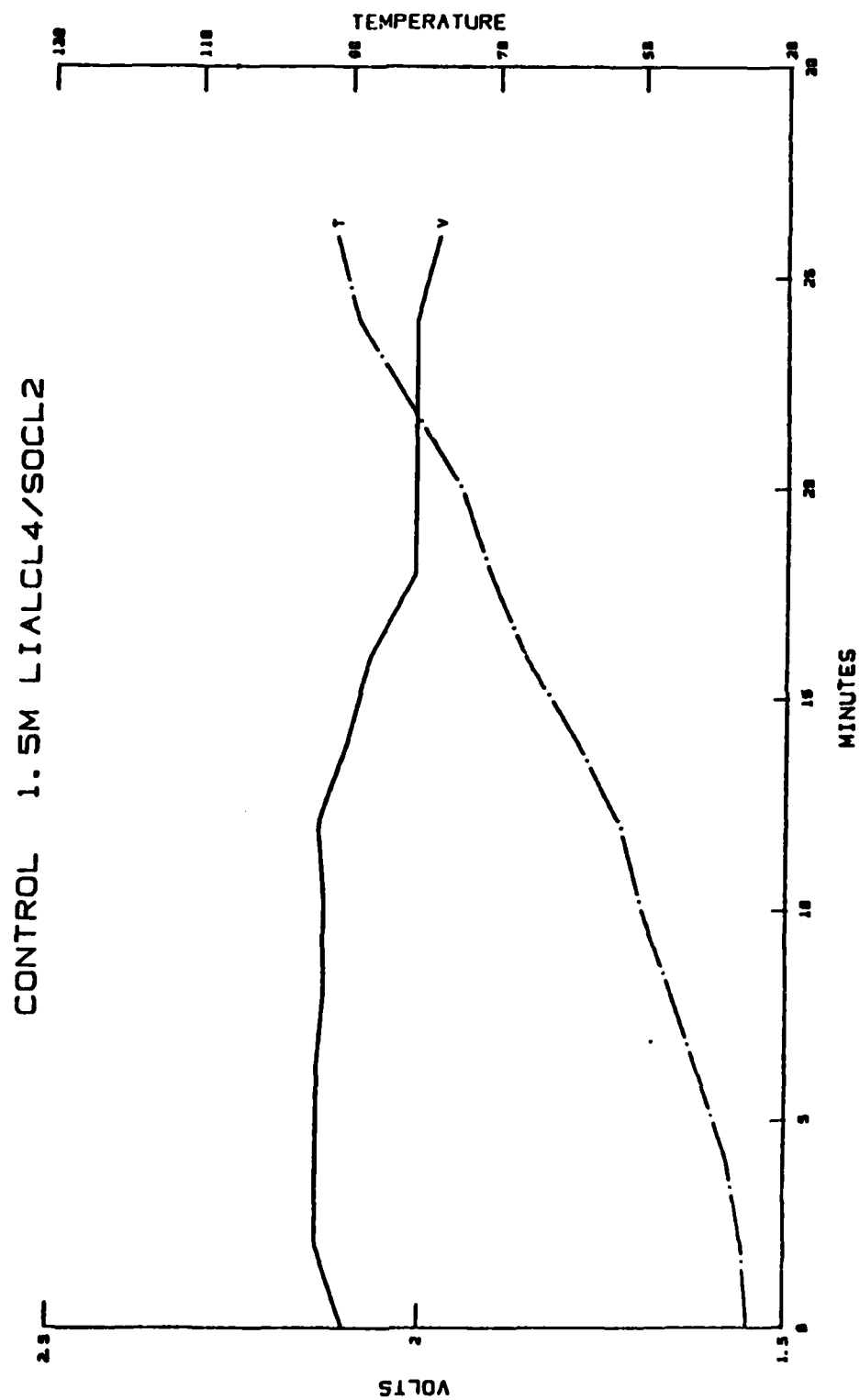


FIGURE 66 Control Cell No. 1 - 1.5 M LiAlCl₄

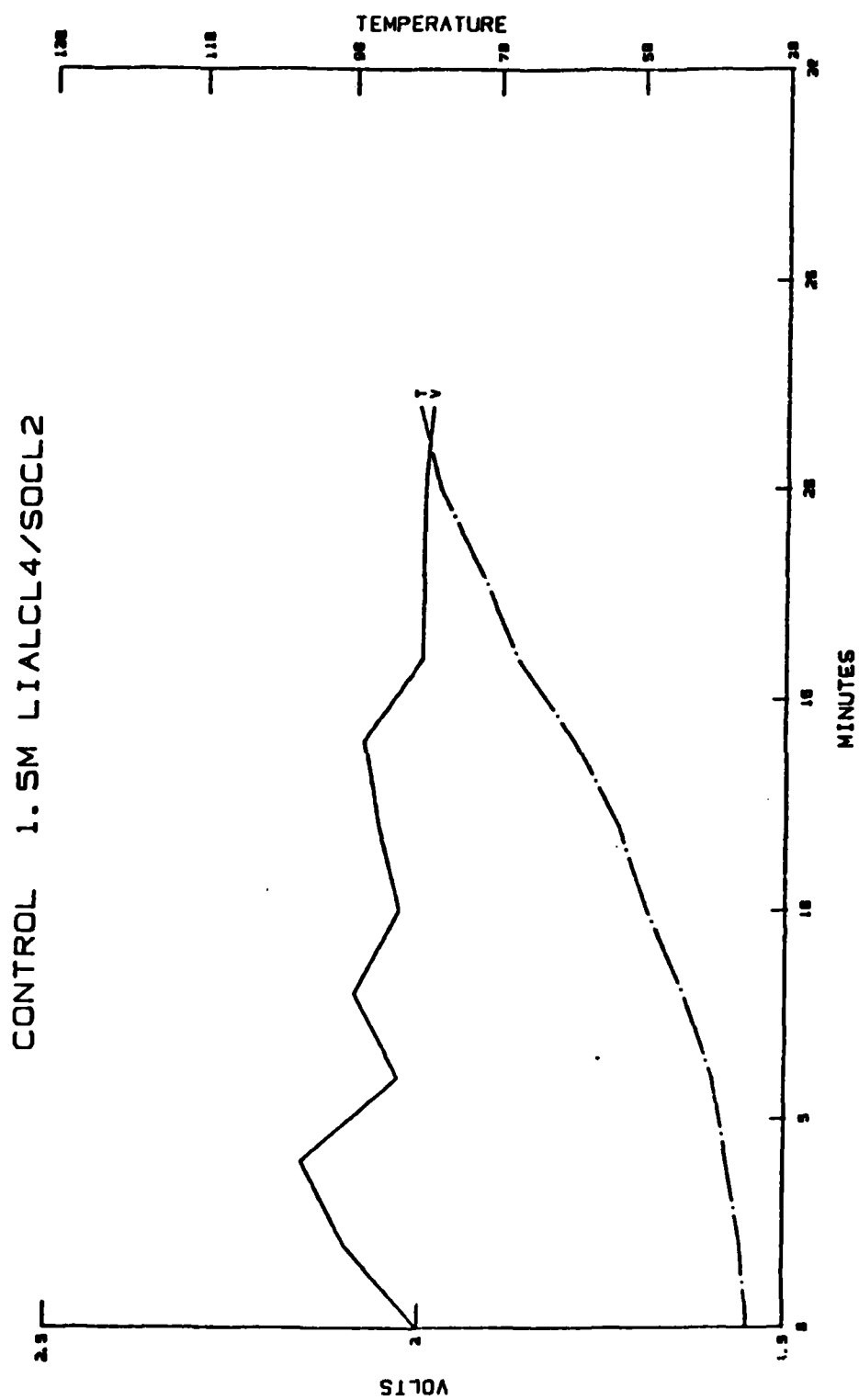


FIGURE 67 Control Cell No. 2 - 1.5 M LiAlCl_4

It was known from the outset that the 1.5M LiAlCl₄ electrolyte could not carry a constant resistive load with as low an Ohm value as the 2:2/3 electrolyte and still maintain a voltage above 2.0 volts. Consequently, all cells utilizing 1.5M LiAlCl₄ electrolyte were discharged with a manually operated variable resistance. During discharge the cell's load was changed arbitrarily to achieve maximum performance and still maintain 2.0 or greater voltage. This method was employed as a data check against the 2:2/3 electrolyte, while generating the most heat from the cell. See Figures 66, 67, 68-72. Technical data for the cells is given in Table 54. With this in mind, the data will show a low average potential but maximize the other cell discharge data for a 20 minute discharge.

TABLE 54 - TECHNICAL DATA FOR FIGURES 68-72

<u>Figure</u>	<u>68</u>	<u>67</u>	<u>70</u>	<u>71</u>	<u>72</u>
\bar{V}	2.01	2.00	2.01	2.00	2.00
VHr	0.67	0.74	0.80	0.73	0.60
AHr	1.38	1.51	1.78	1.53	1.35
AHr/Cm ³	0.06	0.07	0.08	0.07	0.06
Mix	15% Cu	15% Cu Phth	10% Cu Phth	15% Cu Phth	15% Cu
Thickness	0.050"	0.050"	0.050"	0.050"	0.050"
Quantity	15	15	15	15	15
Electrolyte	1.5 LiAlCl ₄	1.5 LiAlCl ₄	1.5 LiAlCl ₄	1.5 LiAlCl ₄	1.5 LiAlCl ₄
Avg. Ohms Load	0.486	0.489	0.451	0.478	0.443
Temp. Max.	83C	73C	65C	72C	71C

AD-A165 657

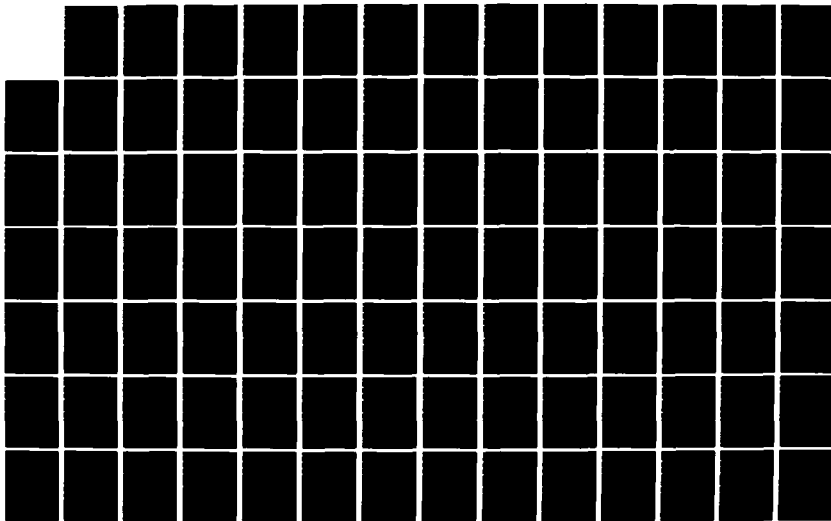
CALCIUM/THIONYL CHLORIDE BATTERY TECHNOLOGY(U)
EAGLE-PICHER INDUSTRIES INC JOPLIN MO ELECTRONICS DIV
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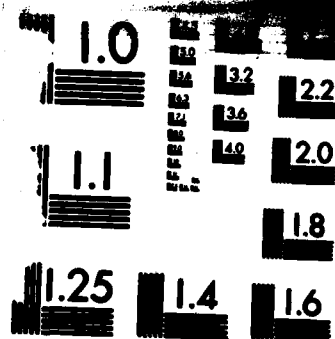
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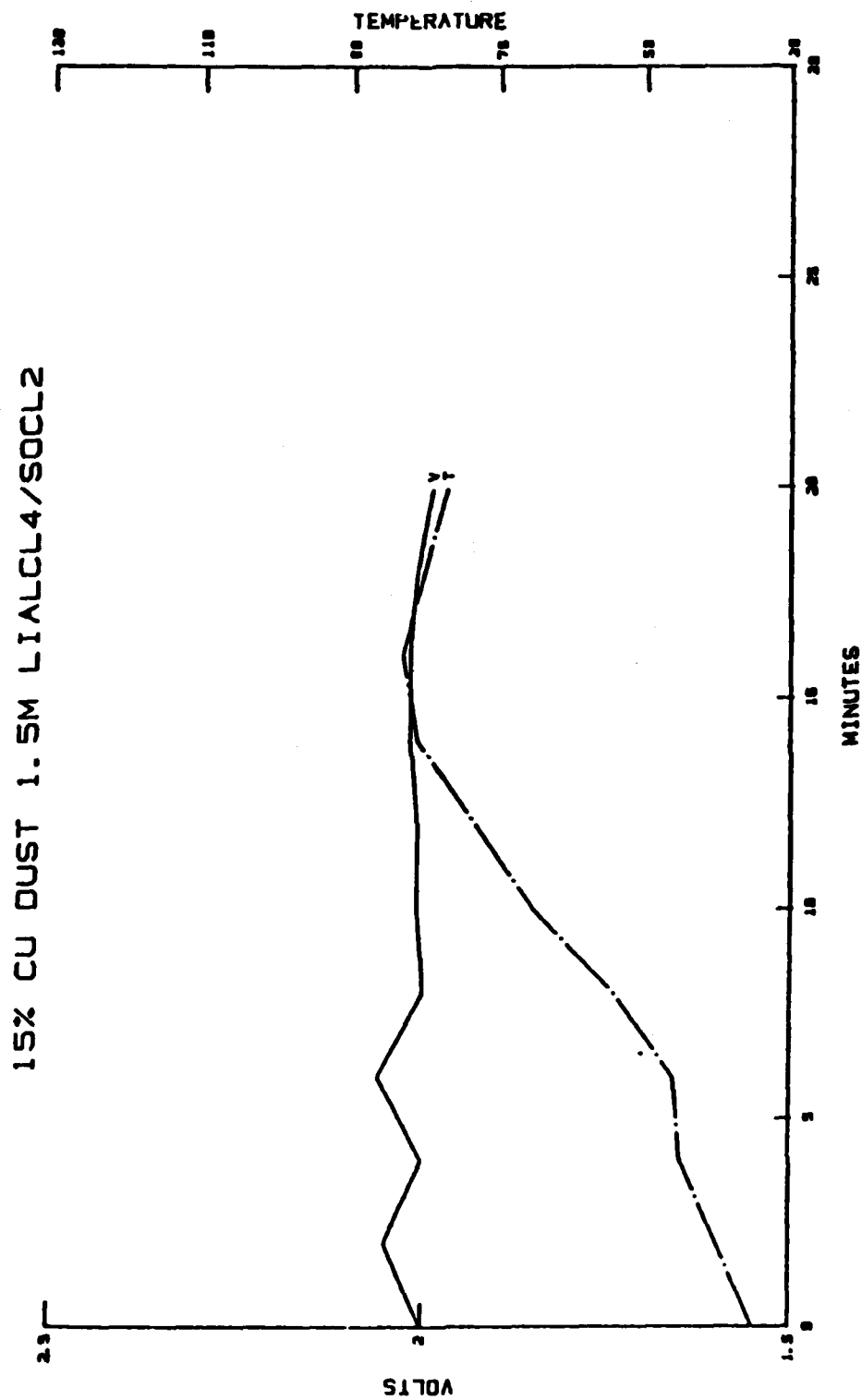


FIGURE 68 No. 1 D-Cell W/15% Cu Cathodes

15% CU PHTH 1.5M LIALCL4/SOCL2

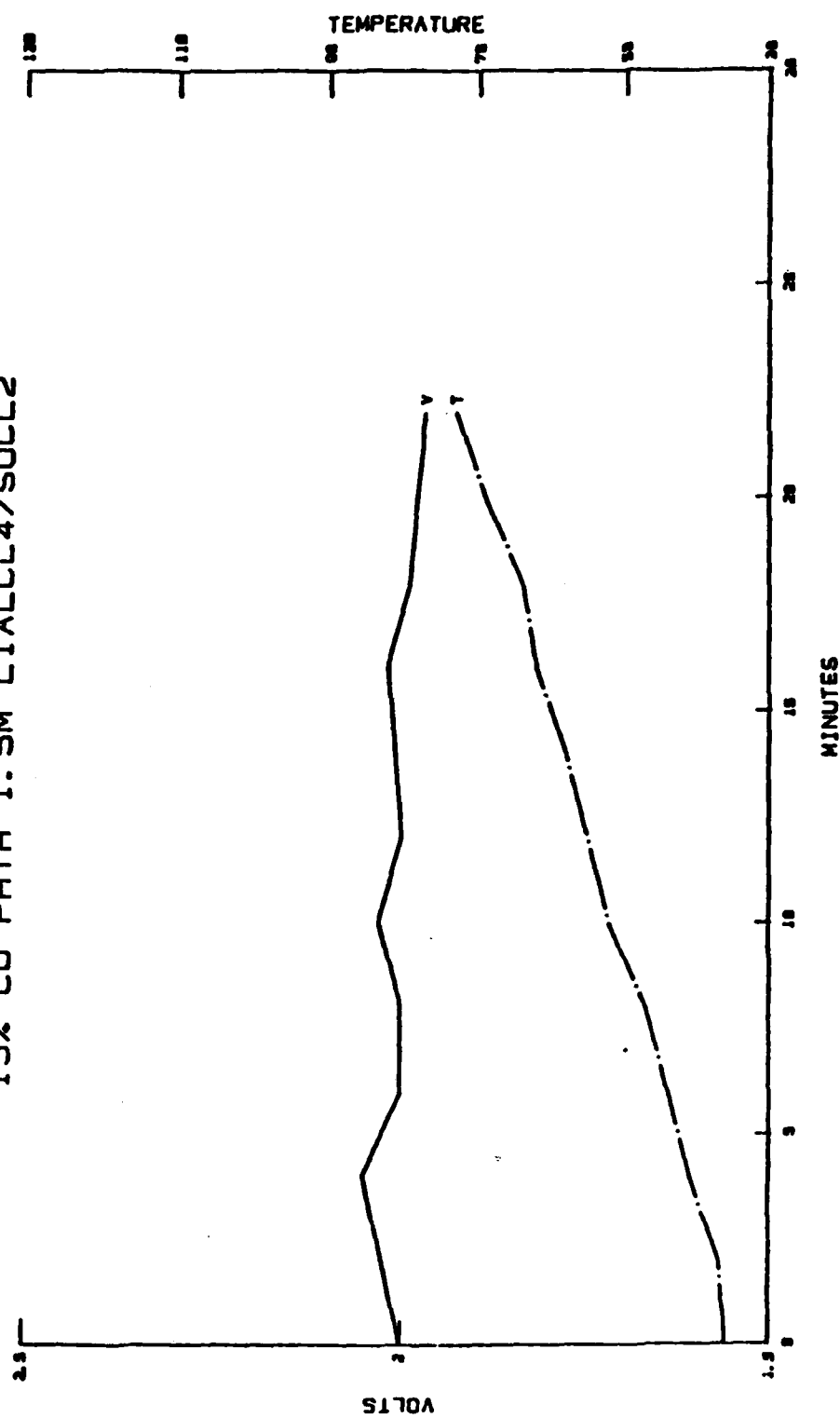


FIGURE 69 No. 1 D-Cell W/15% CuPhth. Cathodes

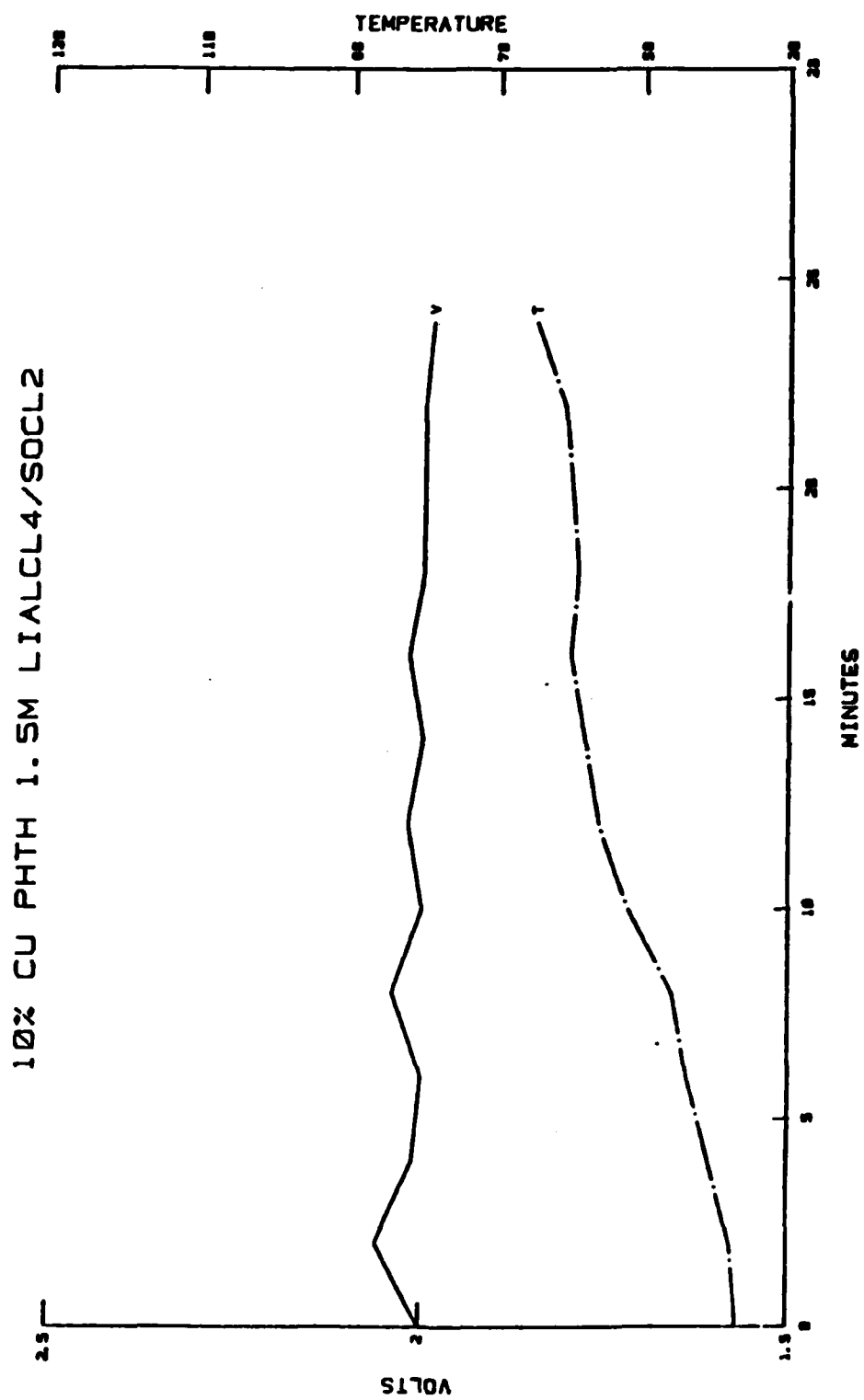


FIGURE 70 D-Cell W/10% Cu Phth. Cathodes

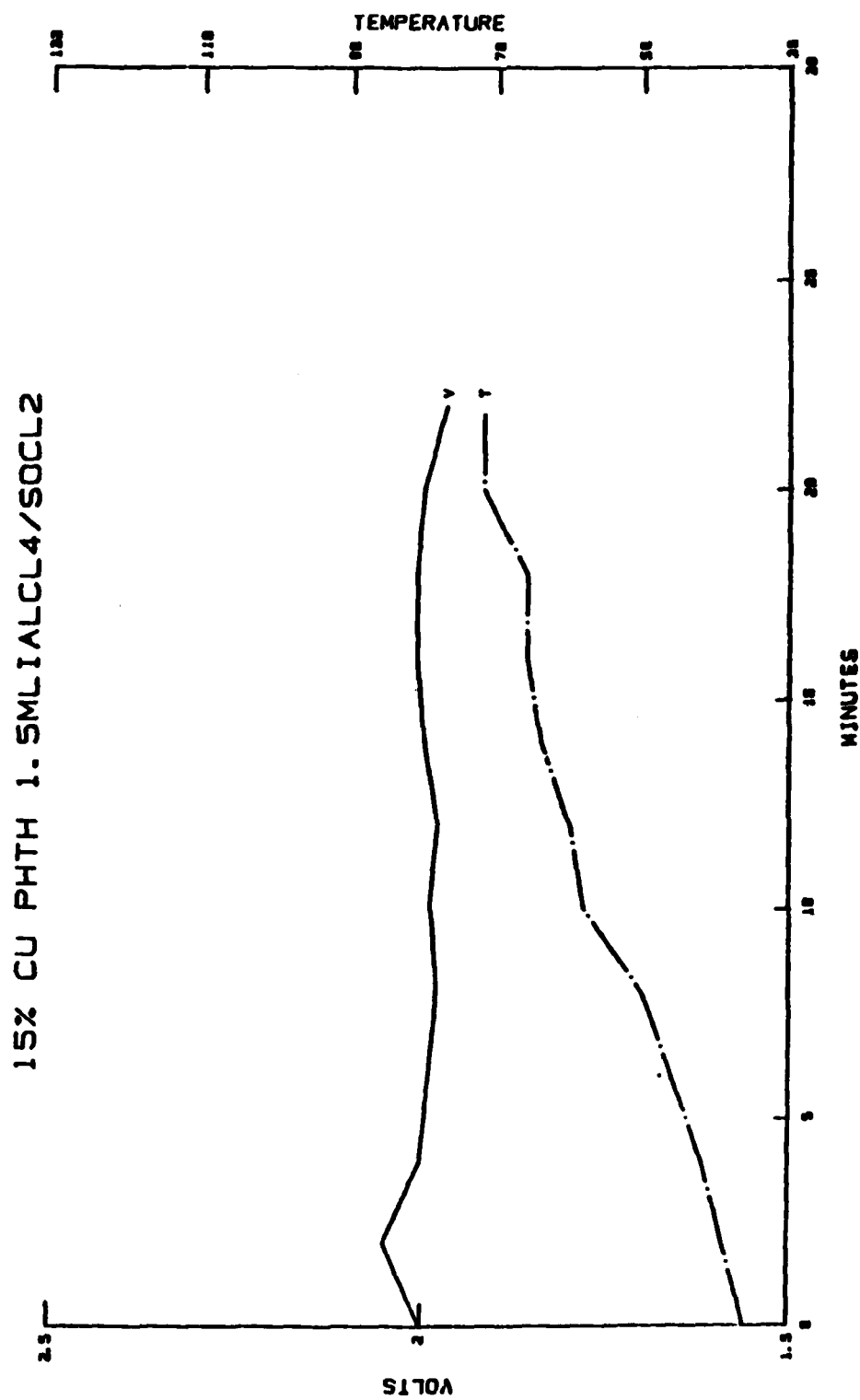


FIGURE 71 No. 2 D-Cell W/15% Cu Phth. Cathodes

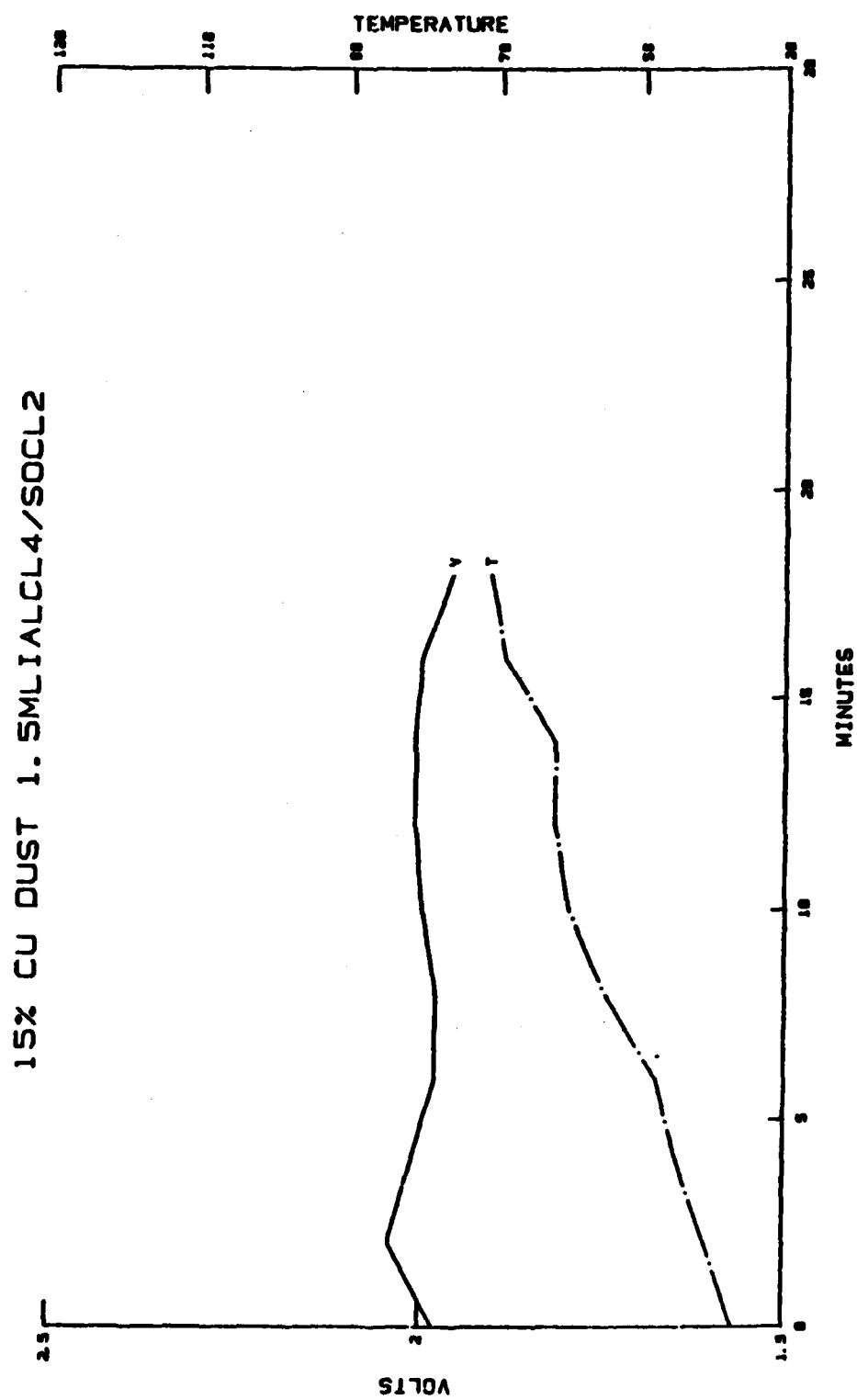


FIGURE 72 No. 2 D-Cell W/15% Cu Cathodes

Stainless steel rectanuglar D-cells were discharged with 2:2/3 electrolyte with Cu Dust and Cu Phth. as cathode additives. The load remained constant throughout the discharge of each individual cell. See Figures 65, 73-77 for discharge curves. Technical data on the cells is given in Table 55

TABLE 55 - TECHNICAL DATA FOR FIGURES 73-77

Figure	73	74	75	76	77
\bar{V}	2.04	2.07	2.07	2.08	2.10
VHr	0.75	0.76	0.83	0.69	1.09
AHr	1.60	1.59	1.89	1.62	2.47
AHr/Cm ³	0.07	0.07	0.08	0.07	0.11
Mix	15% Cu	15% Cu Phth 10% Cu Phth		15% Cu	15% Cu Phth
Thickness	0.050"	0.050"	0.050"	0.050"	0.050"
Quality	15	15	15	15	15
Electrolyte	2:2/3	2:2/3	2:2/3	2:2/3	2:2/3
Ohms Load	0.471	0.477	0.438	0.426	0.440
Temp. Max.	107C	114C	99C	77C	80C

Results of these two series of cells showed that .050 inch thick cathodes coupled with 2:2/3 electrolyte to be as effective as cells constructed with .100 inch thick cathodes using 3:1 electrolyte, while showing less gassing and no higher maximum temperatures reached during discharge. The cells activated with 1.5M LiAlCl₄/SOCl₂ electrolyte performed very similarly to those activated with 2:43 electrolyte, but only at distinctly reduced average loadings.

Discharge life above 2.0V for the cells doped with either Cu dust or Cu Phth did not increase significantly over that achieved by the control cell. Temperature rise was erratic, and more probably reflects variations in degree of cell hermiticity with crimp-seal effectiveness than the effects of the cathode additives.

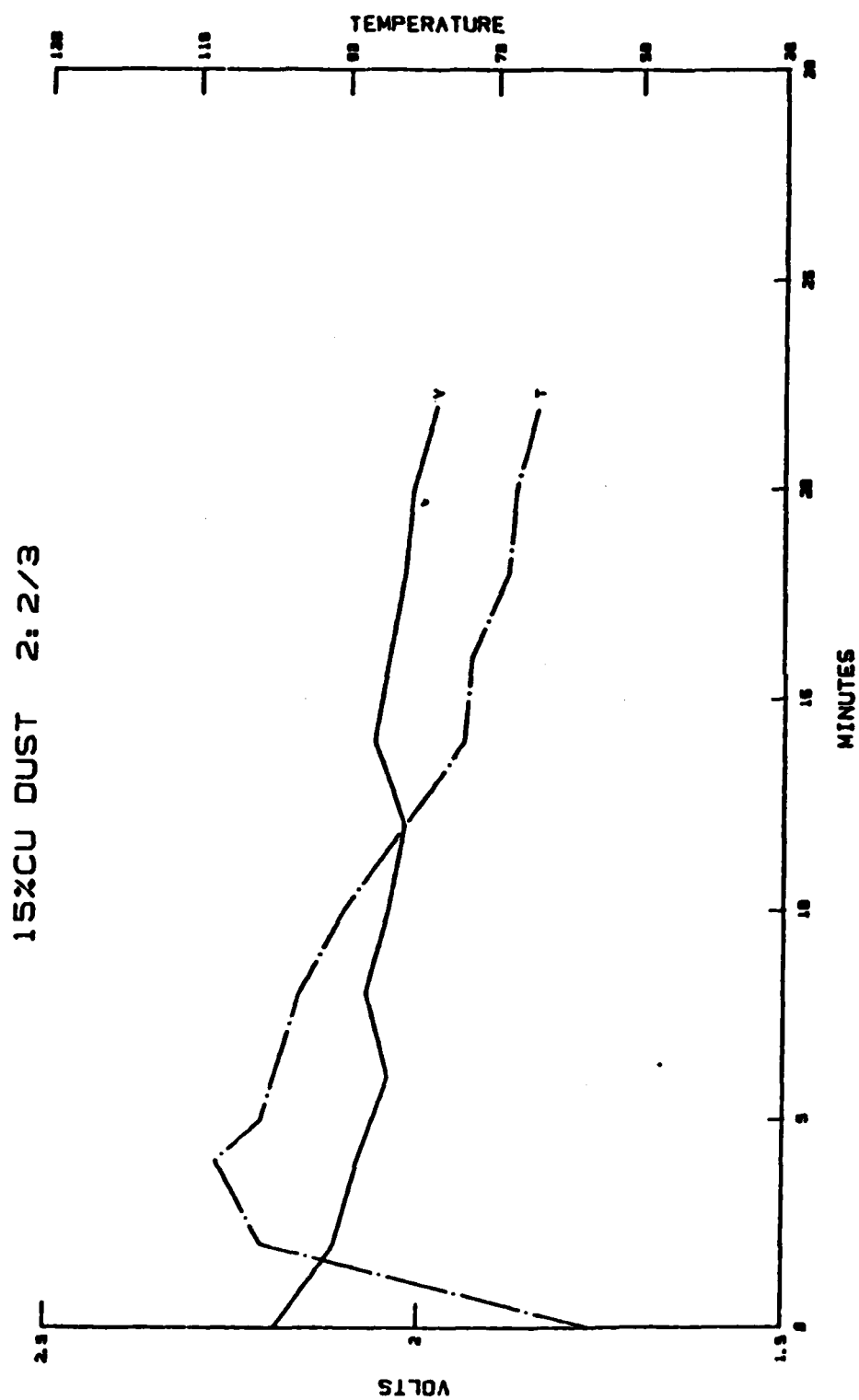


FIGURE 73 No. 3 D-Cell W/15% Cu Cathodes

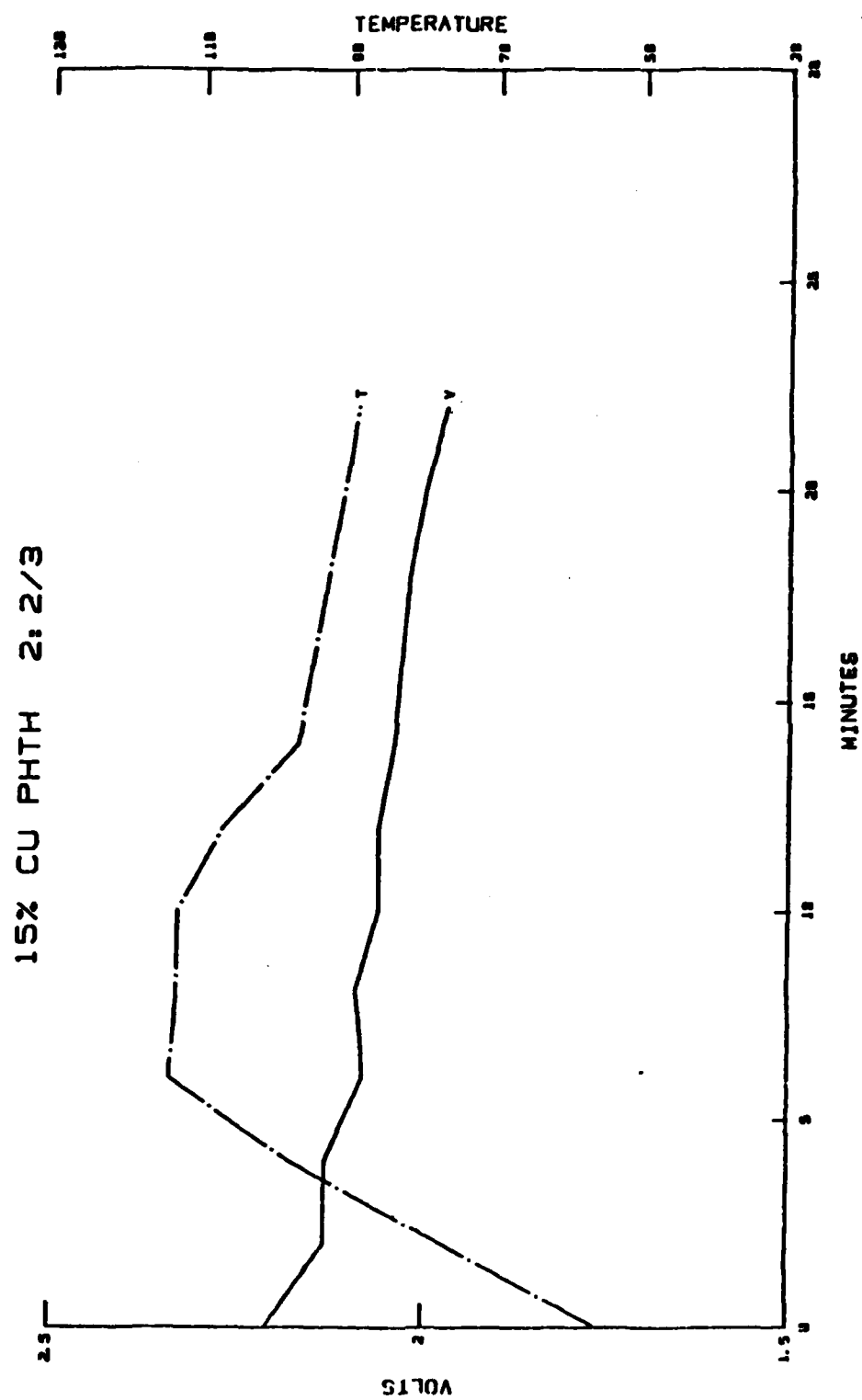


FIGURE 74 No. 3 D-Cell W/15% Cu Phth. Cathodes

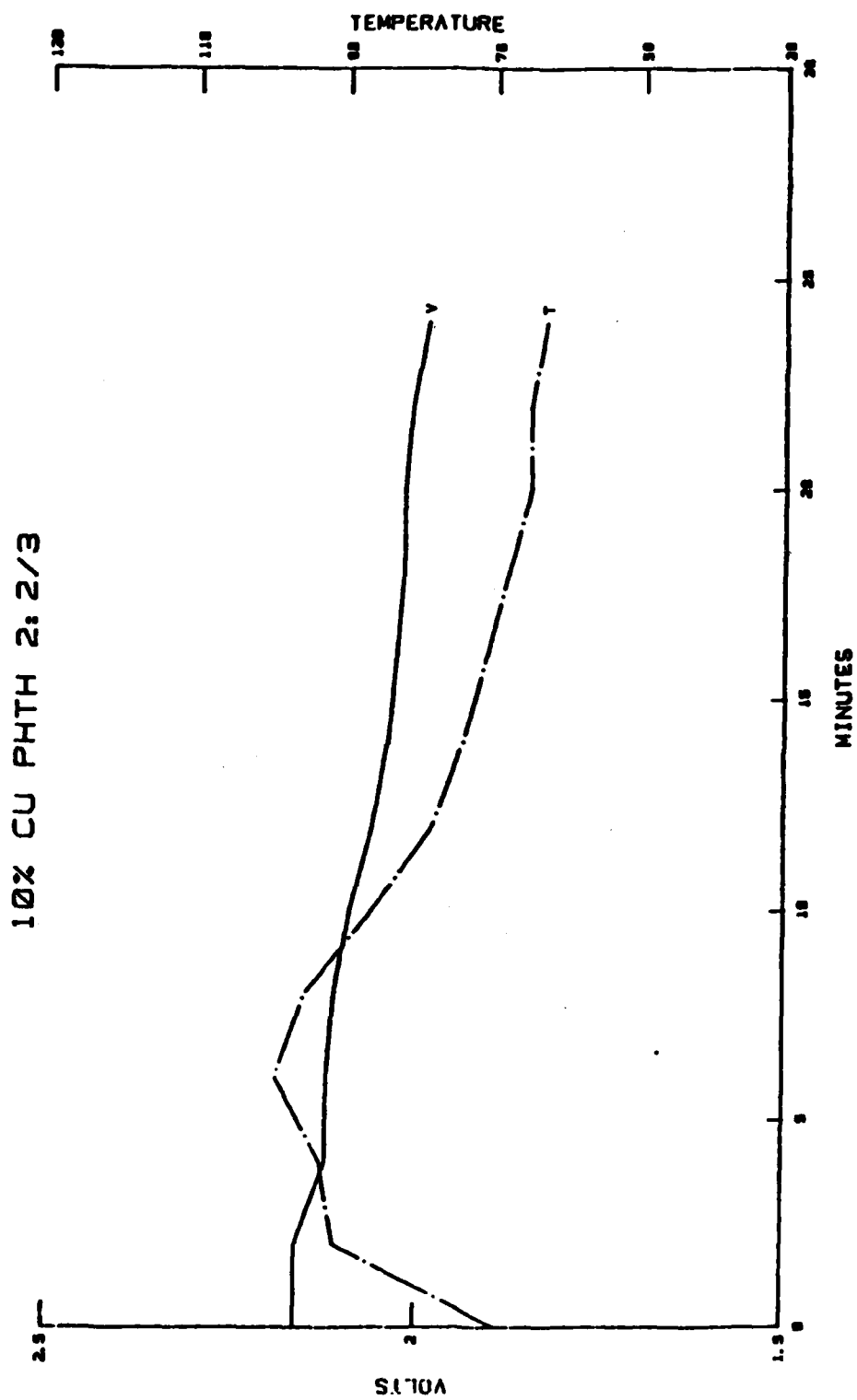


FIGURE 75 No. 2 D-Cell W/10% Cu Phth. Cathodes

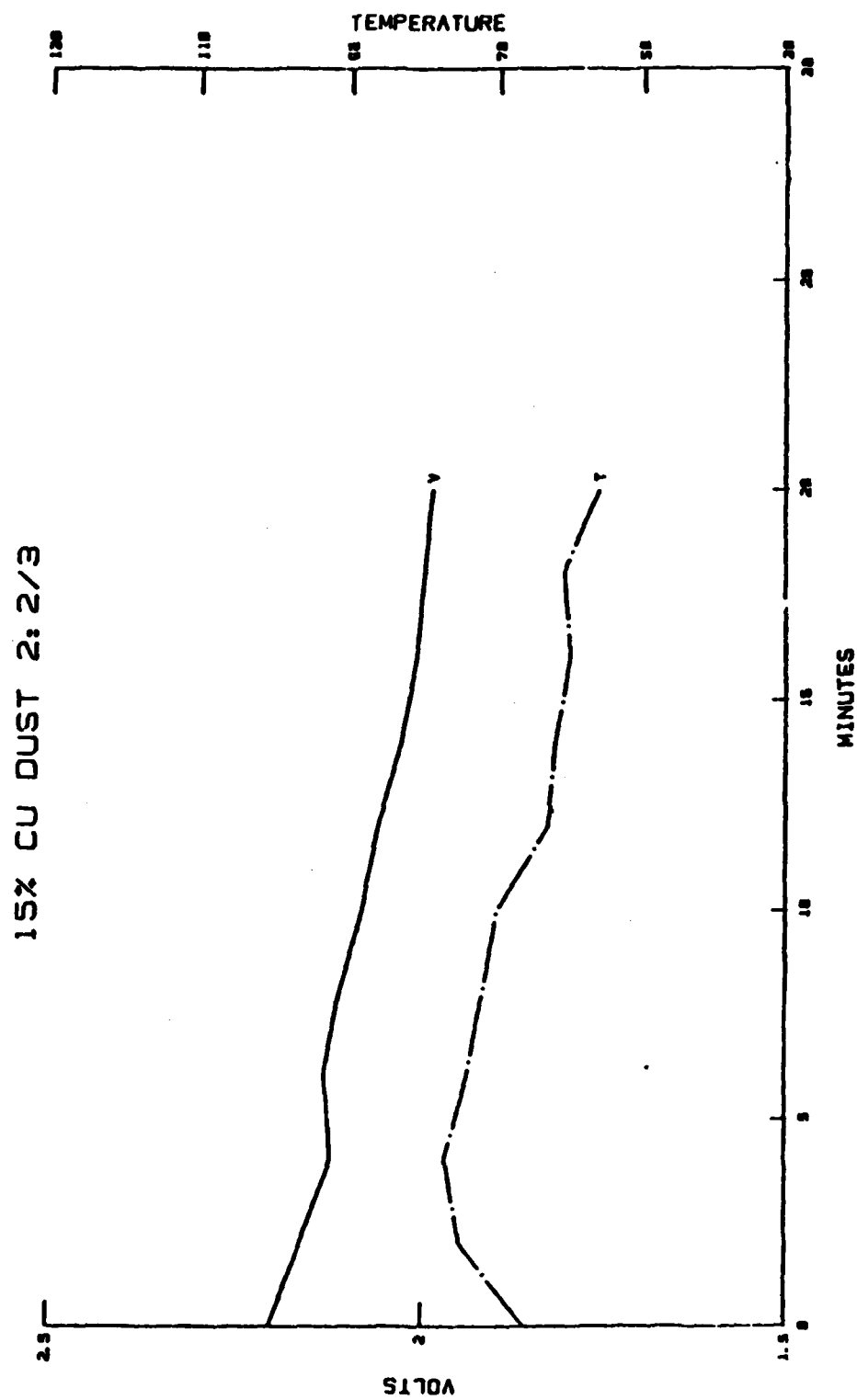


FIGURE 76 No. 4 D-Cell W/15% Cu Cathodes

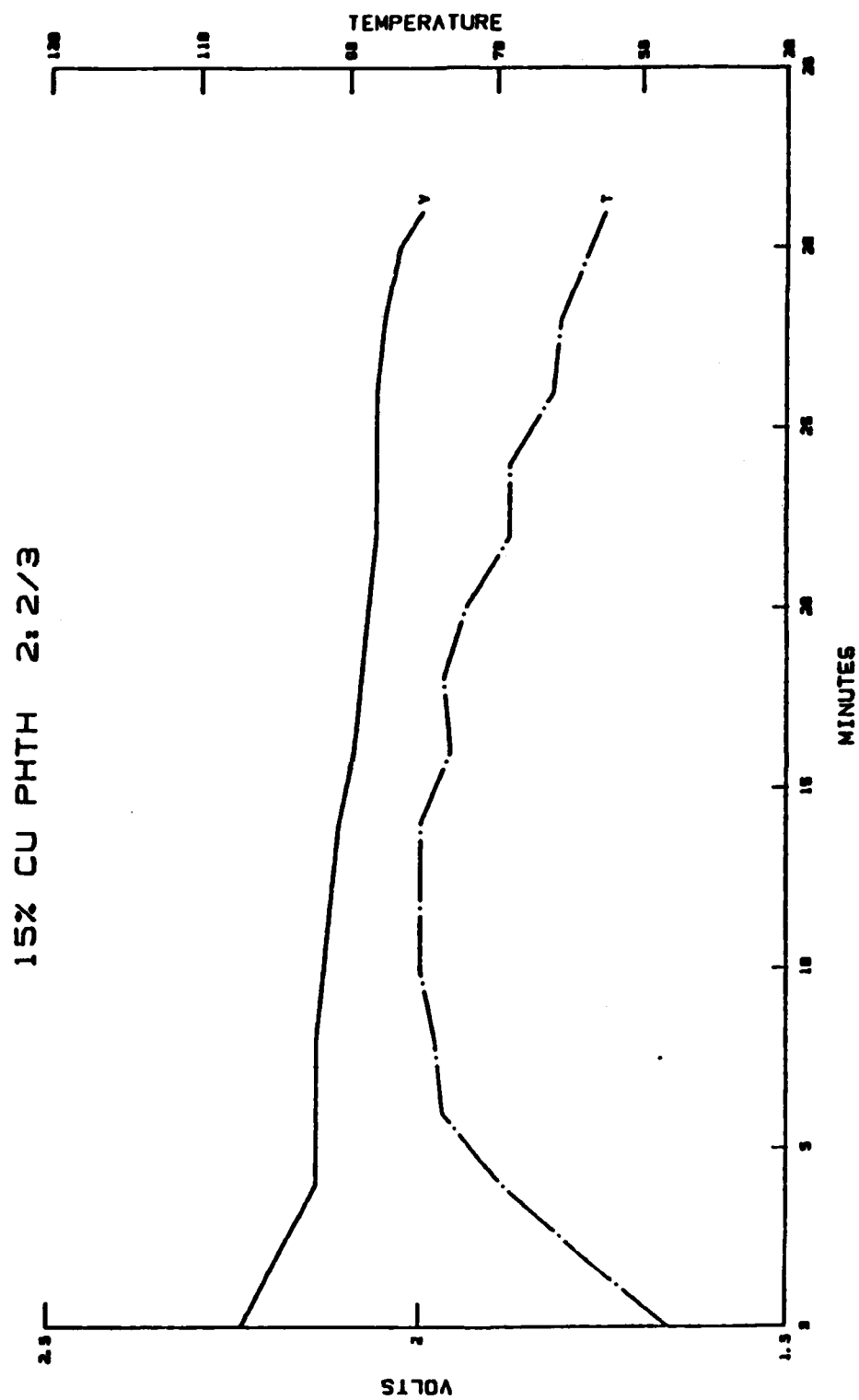


FIGURE 77 No. 4 D-Cell W/15% CuPhth. Cathodes

Autopsies of the cells in this series showed the cathodes to be brittle to semi-brittle, indicative of a completely spent cathode. Most calcium anodes however, showed shiney, relatively untouched centers, an indication of incomplete electrolyte wetting.

One cathode and anode was retrieved from each cell. The set from Figure 71, Table 54 was randomly chosen, and placed in an unrestrained bag cell. The bag cell was activated with app. 18 ml of 2:2/3 electrolyte and discharged with a constant resistive load of 4.2 ohm (31 mA/cm^2), twice the current density on D-cells bring discharged. The load was left connected for 55 minutes at an average 3.12 voltage. Cathode size was 1" x 1.875" x 0.050". This serves to verify that the cells were electrolyte limited.

11.4 CuCl₂ Cathode Additive

A matrix of stainless steel rectangular D-cells was constructed to evaluate the effects of cupric chloride (CuCl₂) as a cathode additive and to compare the performance of 2:2 versus 2:2/3 electrolyte. Technical cell data and discharge summation data are given in Table 56. Discharge curves for the cells are given as Figures 78 to 83. The cathodes were prepared by dry pressing the standard cathode mix, containing 10% CuCl₂, at 1200 psi. Each cathode measured 1"x1.875"x.050". The load employed for the cells was manually varied to keep the discharge time as close to 21 minutes as possible without driving the load voltage below 2.0. This makes comparison between this and other cells matrices in the series difficult. However, within this matrix, the CuCl₂ showed a tendency to hold discharge temperatures to a somewhat lower level than the cells without the cathode addition. This must be balanced against a lower average amp-hour total above 2.0 volts and at a slightly lower load level. The 2:2 electrolyte performed at a very similar level to cells from the previous series that utilized 2:43 electrolyte.

TABLE 56 - CATHODE ADDITIVE DATA FOR FIGURES 78-83

<u>Figure</u>	<u>78</u>	<u>79</u>	<u>80</u>	<u>81</u>	<u>82</u>	<u>83</u>
Discharge Min.	21	20	20	20	21	21
\bar{V}	2.09	2.12	2.06	2.02	2.01	2.02
VHr	0.70	0.70	0.69	0.67	0.67	0.67
AHr	1.74	1.86	1.72	1.77	1.86	1.92
AHr/cm ³	0.075	0.081	0.075	0.077	0.081	0.083
Watt Hr	3.64	3.94	3.54	3.57	3.74	3.88
mA/cm ² (Avg.)	14.4	15.4	14.2	14.6	15.4	15.9
Cath. Mix	10% CuCl	10% CuCl	10% CuCl	10% CuCl	Control	Control
Thickness	0.050"	0.050"	0.050"	0.050"	0.050"	0.050"
Quality	15	15	15	15	15	15
Electrolyte	2:2/3	2:2/3	2:2	2:2	2:2	2:2
Avg. Ohms Load	0.40	0.38	0.40	0.38	0.36	0.35
Temp. Max.	73C	70C	70C	69C	79C	95C

11.5 Duplication-Original D-cell

3.2 in³ D-cells and 7.5 in³ Rectcells were fabricated to duplicate the original D-cells which attained 7 amps during discharge with an average voltage of approximately 2.3 volts. The D-cells were constructed with 5 cathodes, standard mix, 1" x 1.875" x 0.150", 0.050" Ca anodes and Dexter separator. The 7.5 in³ Rectcells were fabricated under the same parameters to check if the Rectcell results were proportional to the D-cell results according to the increased size of the cathode. The Rectcells were fabricated with 5 cathodes, standard mix, 2.250"x2.125"x0.150", 0.010" Ca anodes, Dexter separator.

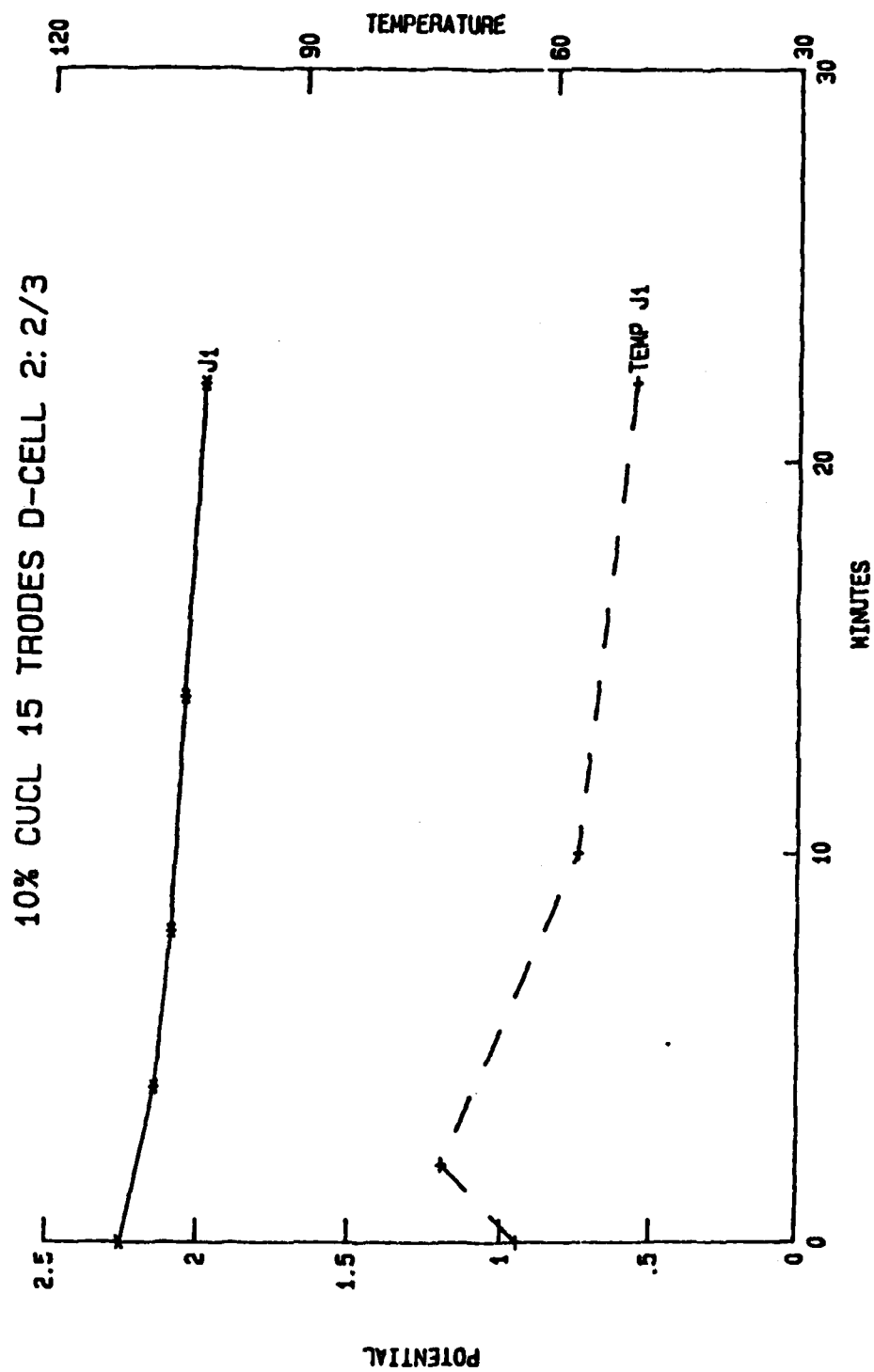


FIGURE 78 No. 1 D-Cell w/10% CuCl₂ Cathodes

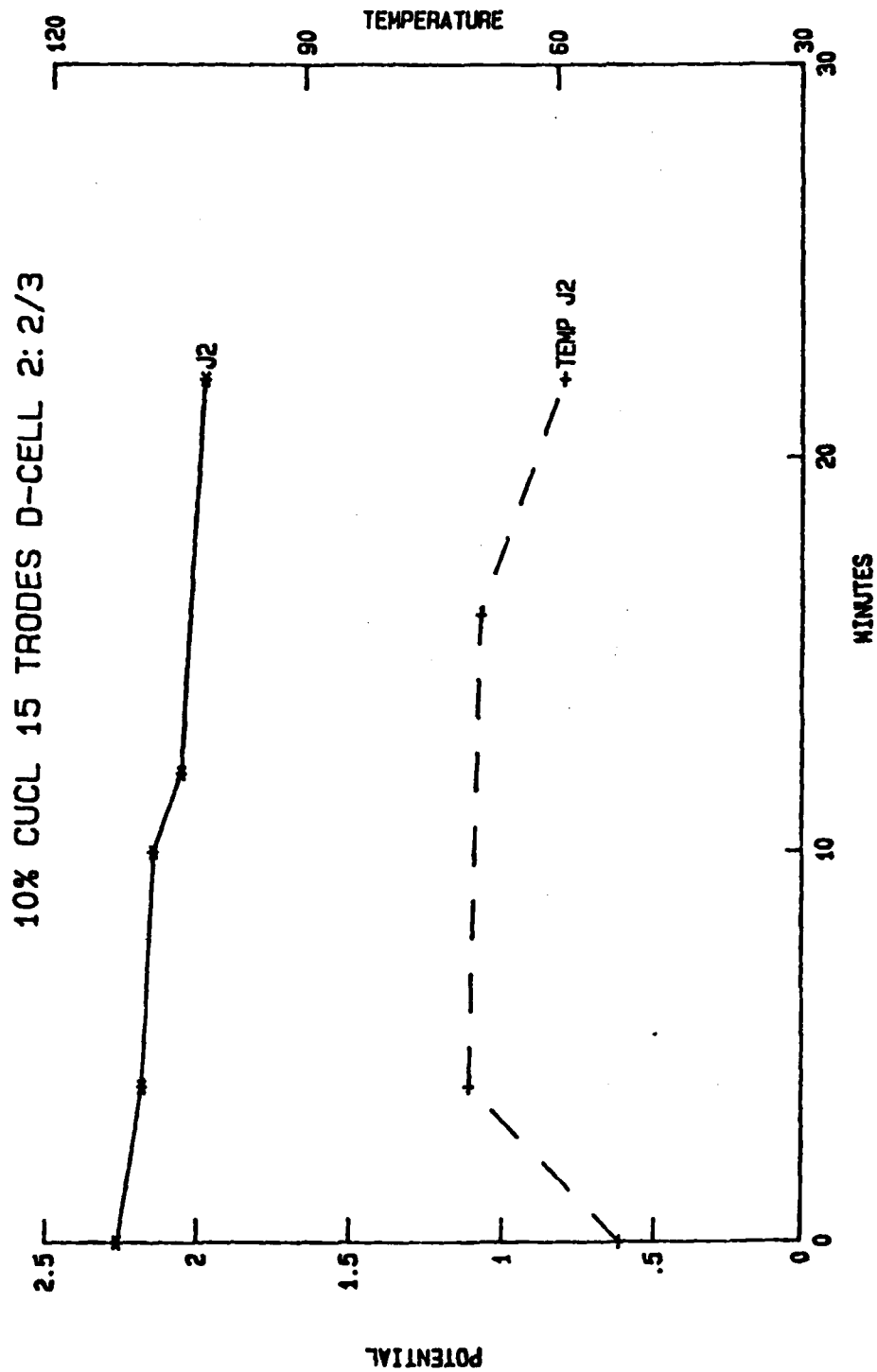


FIGURE 79 No. 2 D-Cell W/10% CuCl₂ Cathodes

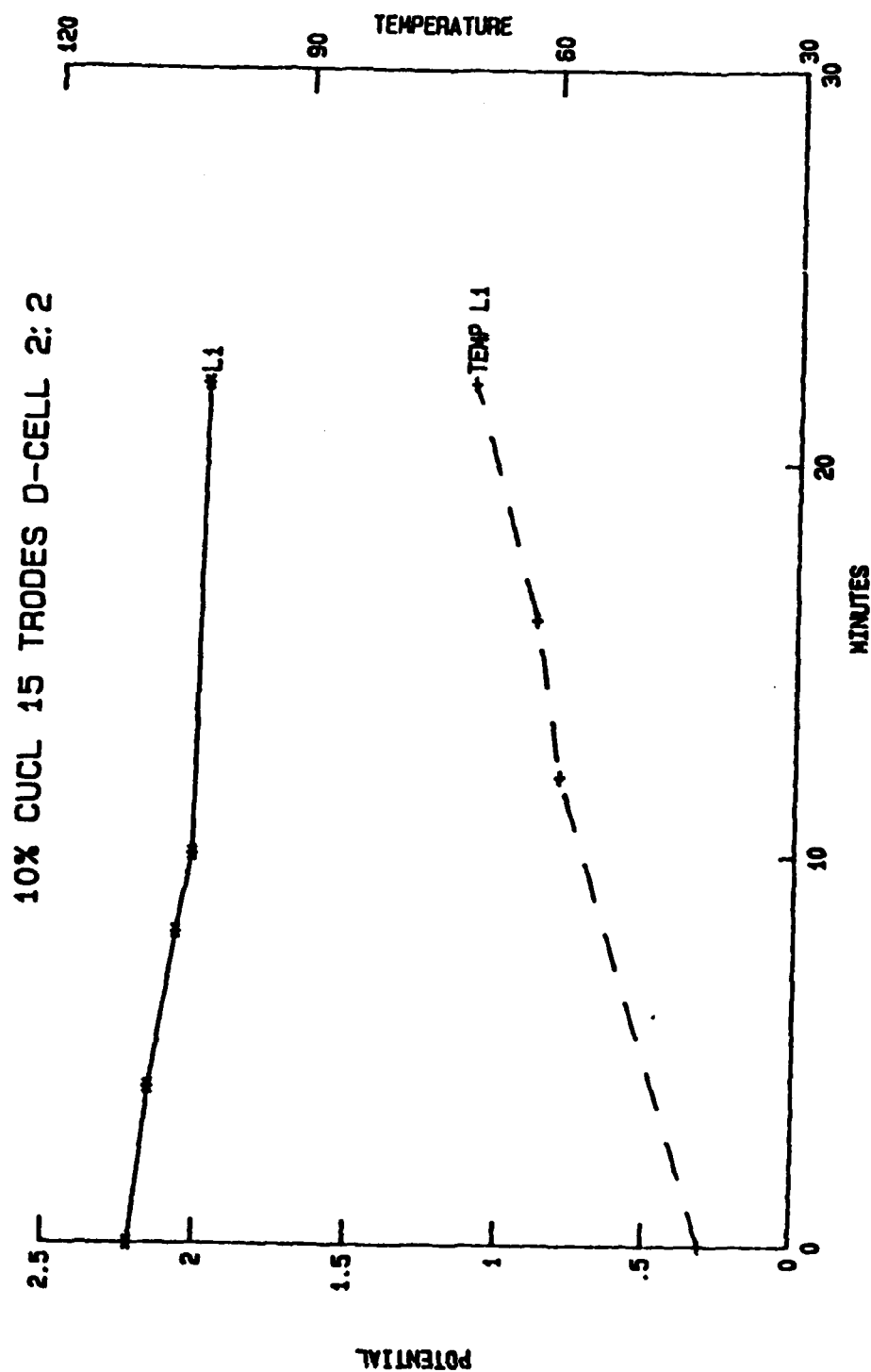


FIGURE 80 No. 3 D-Cell W/10% CuCl_2 Cathodes

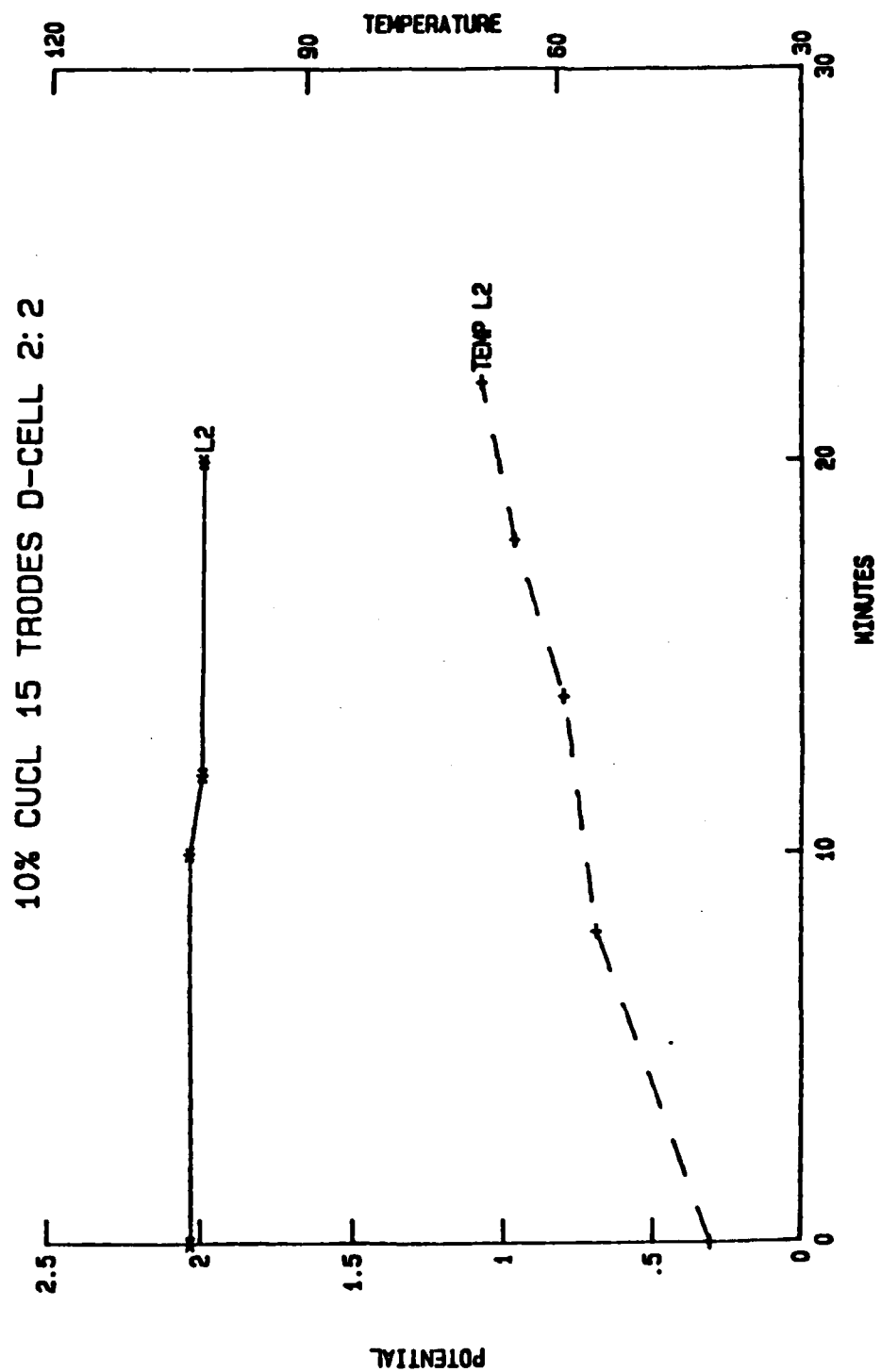


FIGURE 81 No. 4 D-Cell W/10% CuCl₂ Cathodes

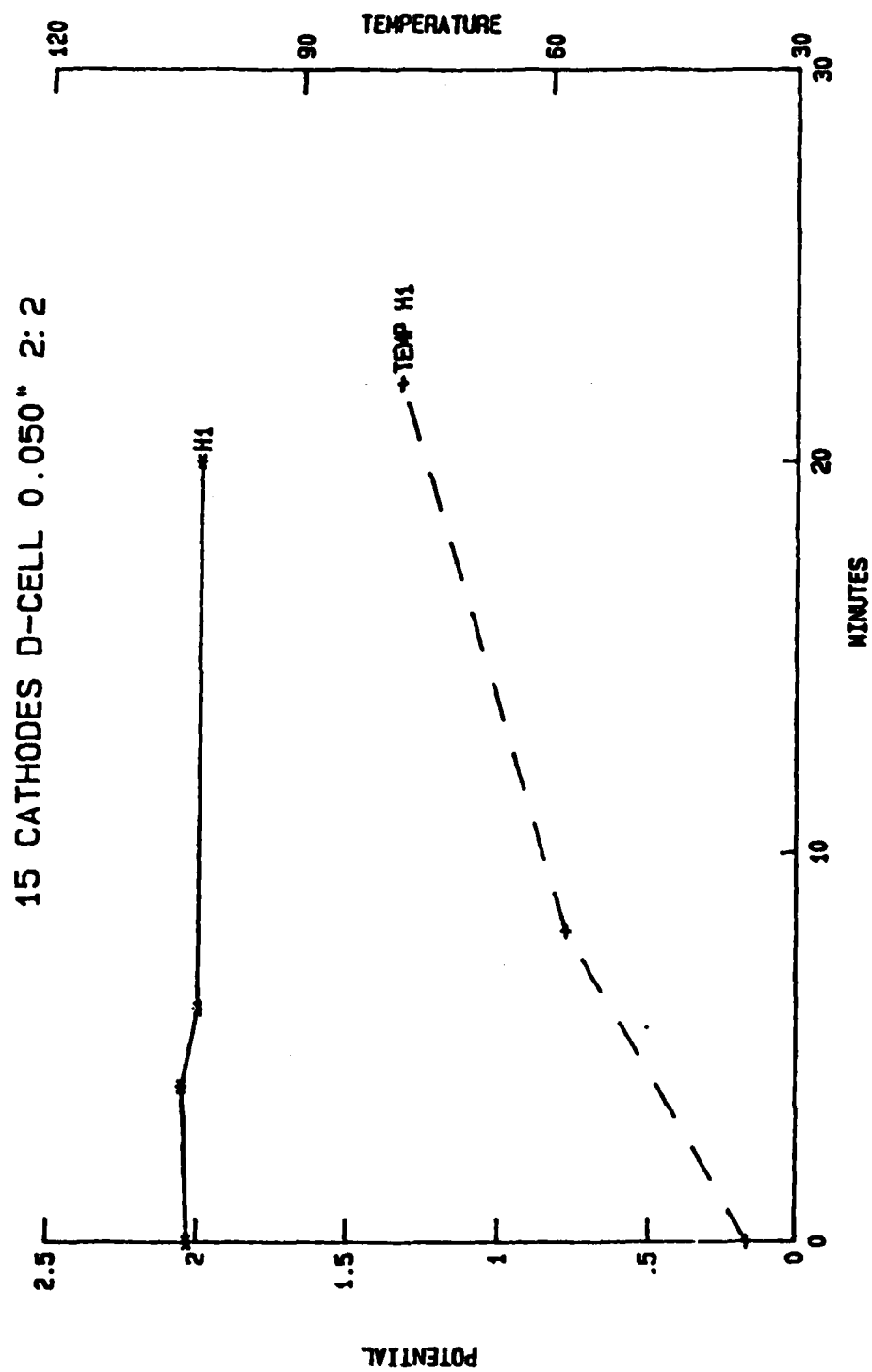


FIGURE 82 Control Cell No. 1

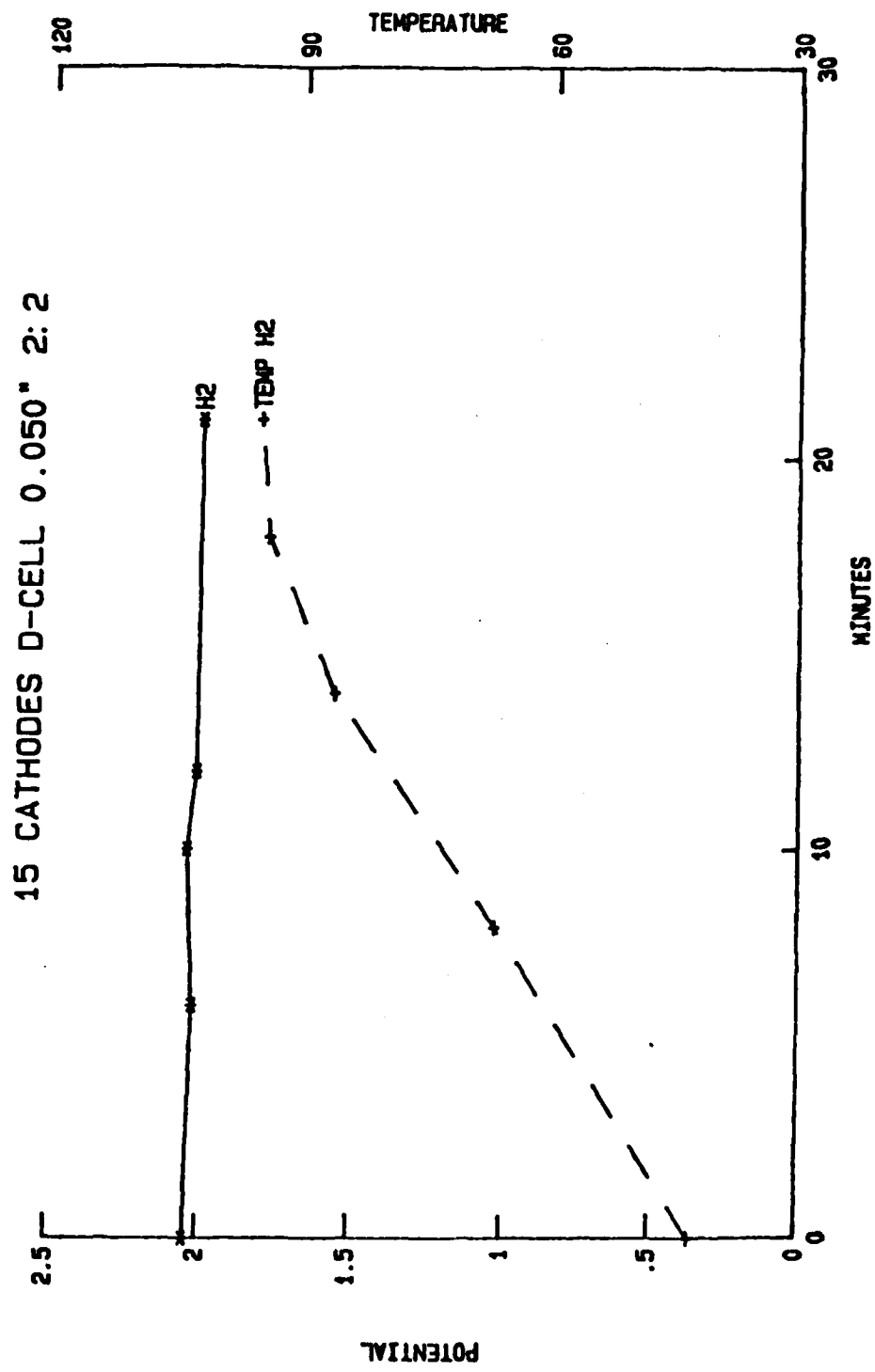


FIGURE 83 Control Cell No. 2

The D-cells were discharged using 3:1 electrolyte, 2:2 electrolyte, 2:2/3 electrolyte. The Rectcells were discharged using 2:2 electrolyte and 2:2/3 electrolyte. Two trials were run at each of the electrolyte concentrations. Technical and discharge data on the D-cells are given in Table 57. Discharge curves are given in Figures 84-89. Technical and discharge data on the Rectcells are given in Table 58. Discharge curves for the cells are given as Figures 90 and 91.

TABLE 57 - D-CELL TECHNICAL DATA FOR FIGURES 84-89

<u>Figure</u>	<u>84</u>	<u>85</u>	<u>86</u>	<u>87</u>	<u>88</u>	<u>89</u>
Discharge Min.	17	19	28	28	27	23
\bar{V}	2.09	2.16	2.09	2.10	2.14	2.05
VHr	0.63	0.72	0.70	0.70	0.71	0.68
AHr	1.03	1.07	0.97	1.00	1.30	1.20
AHr/cm ³	0.045	0.046	0.042	0.043	0.056	0.052
Watt Hr	2.15	2.31	2.03	2.10	2.78	2.46
mA/cm ² (Avg.)	28.3	26.6	24.0	24.8	32.2	29.7
Cat. Mix	Std	Std	Std	Std	Std	Std
Thickness	0.150"	0.150"	0.150"	0.150"	0.150"	0.150"
Quantity	5	5	5	5	5	5
Electrolyte	3:1	3:1	2:2	2:2	2:2/3	2:2/3
Avg. Ohms load	0.61	0.67	0.72	0.70	0.55	0.57
Temp. Max.	46C	51C	45C	46C	58C	58C

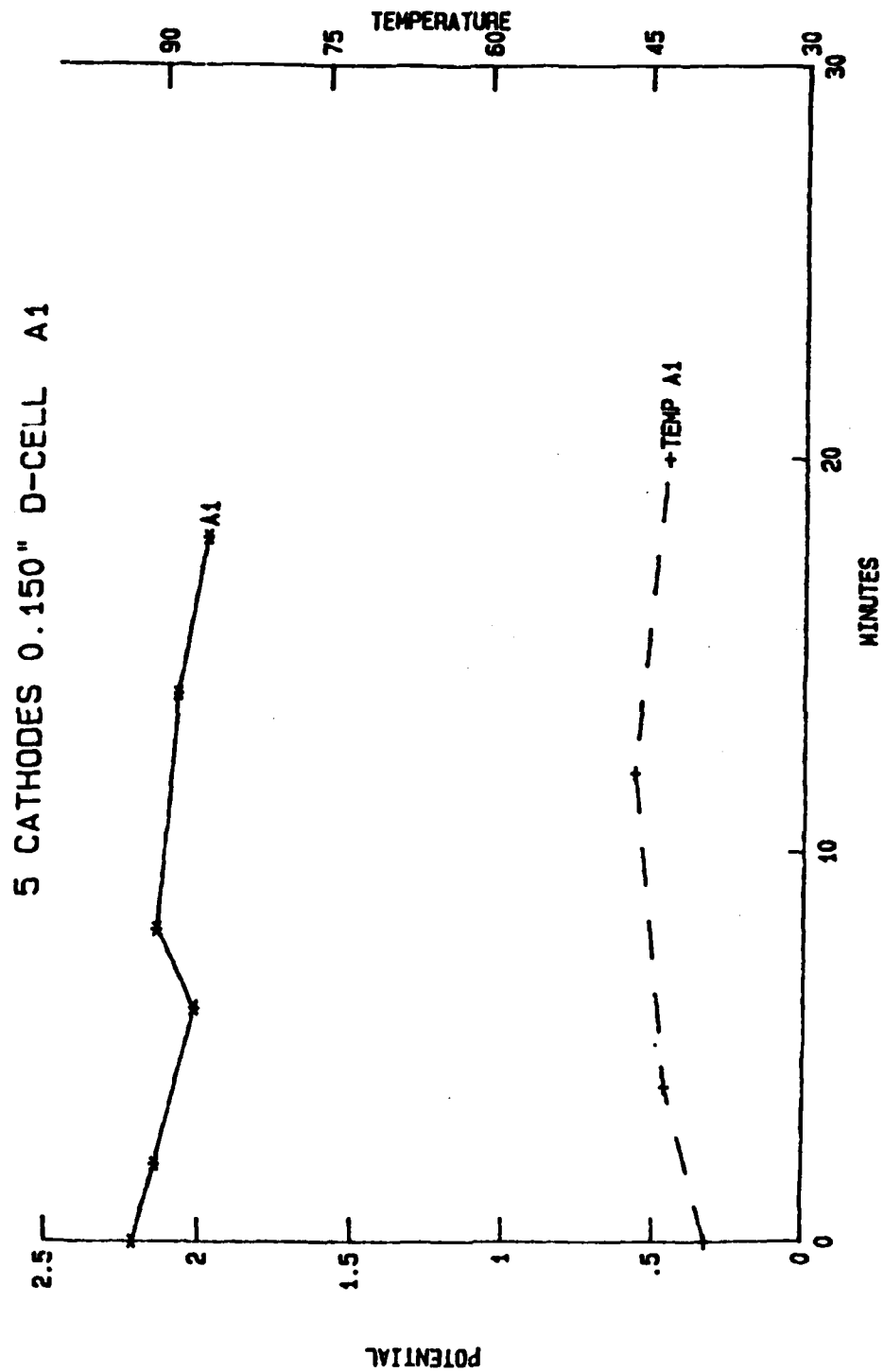


FIGURE 84 No. A1 D-Cell-Original Configuration

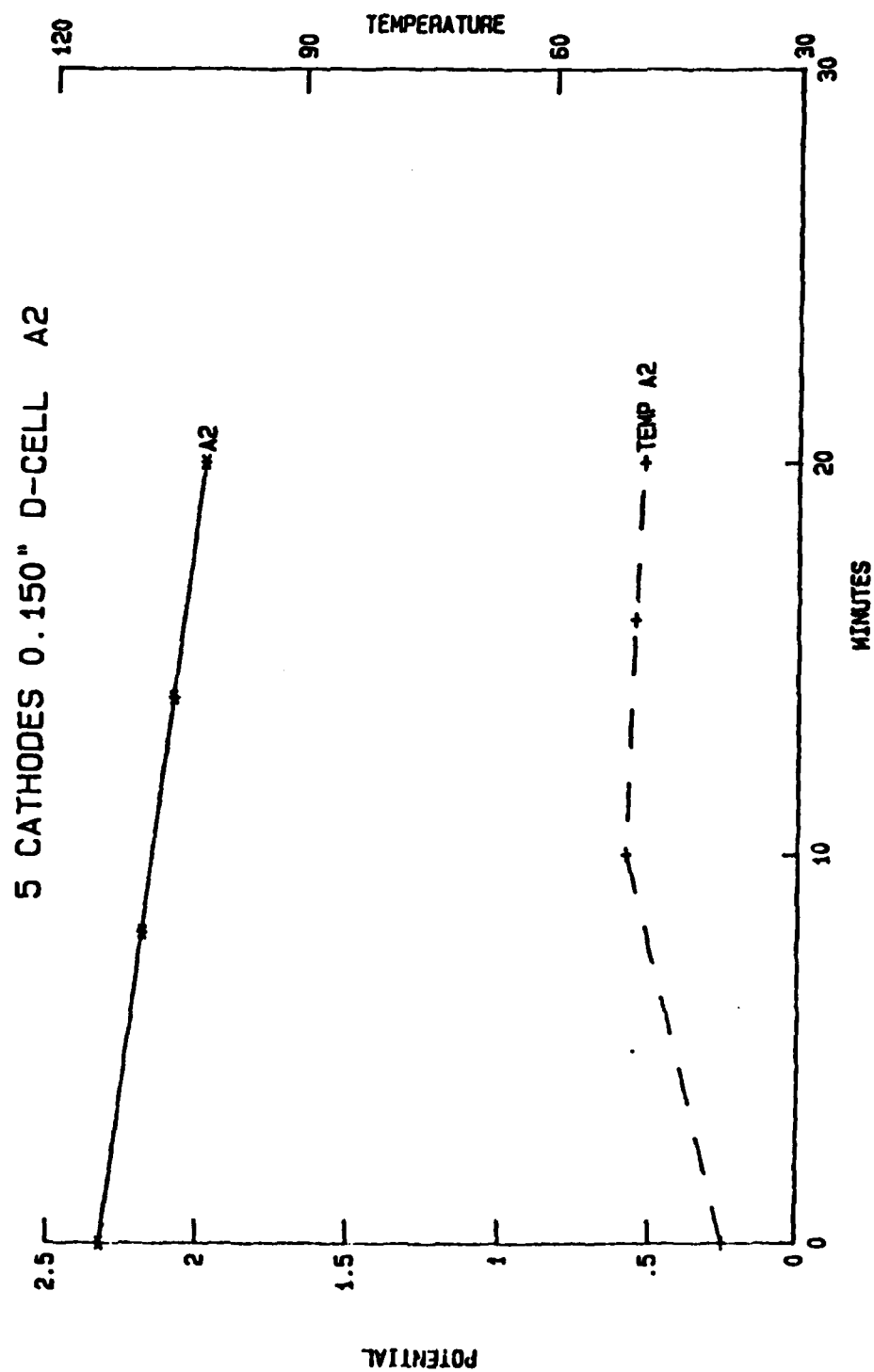


FIGURE 85 No. A2 D-Cell-Original Configuration

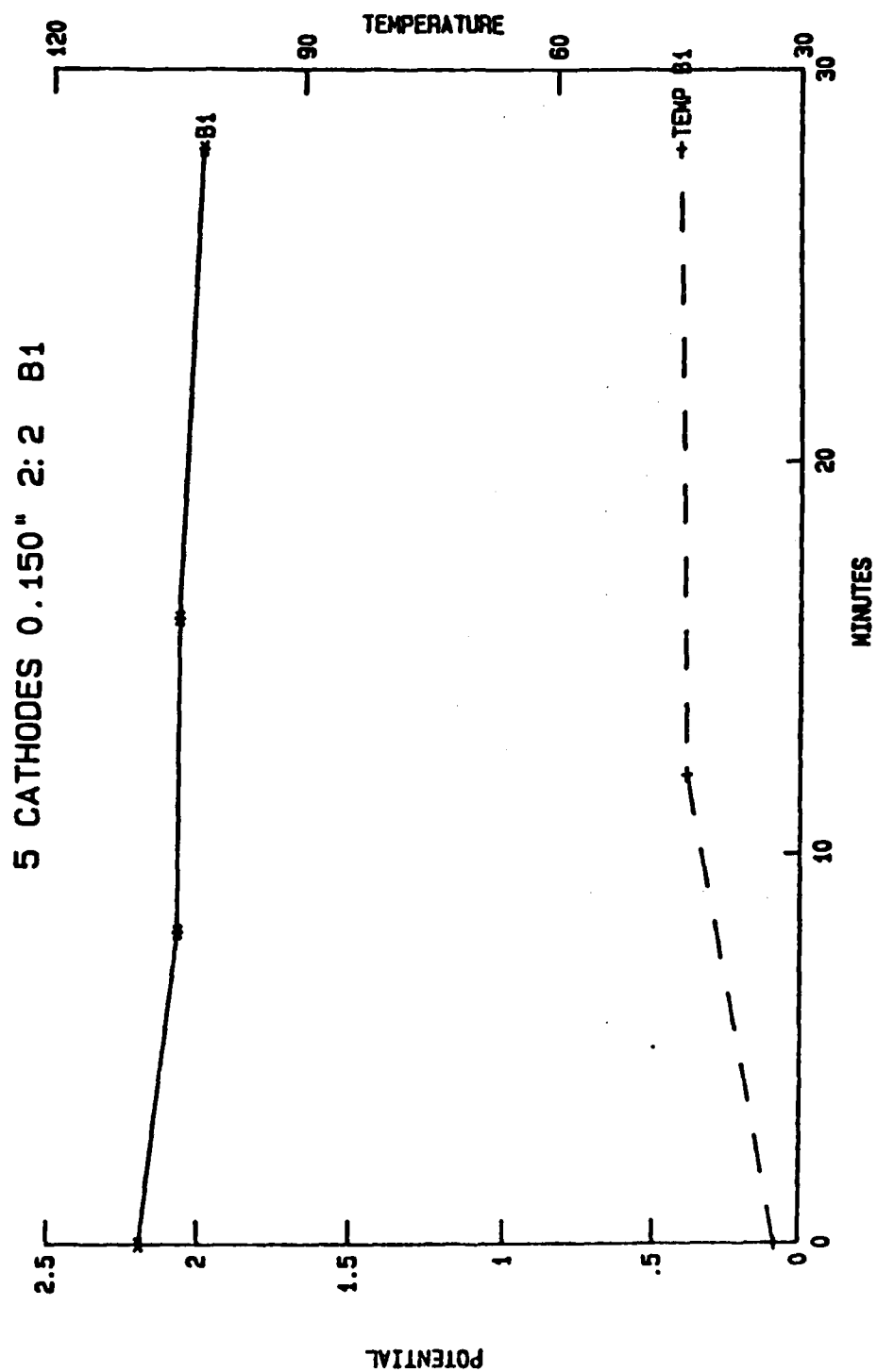


FIGURE 86 B1 D-Cell-Original Configuration

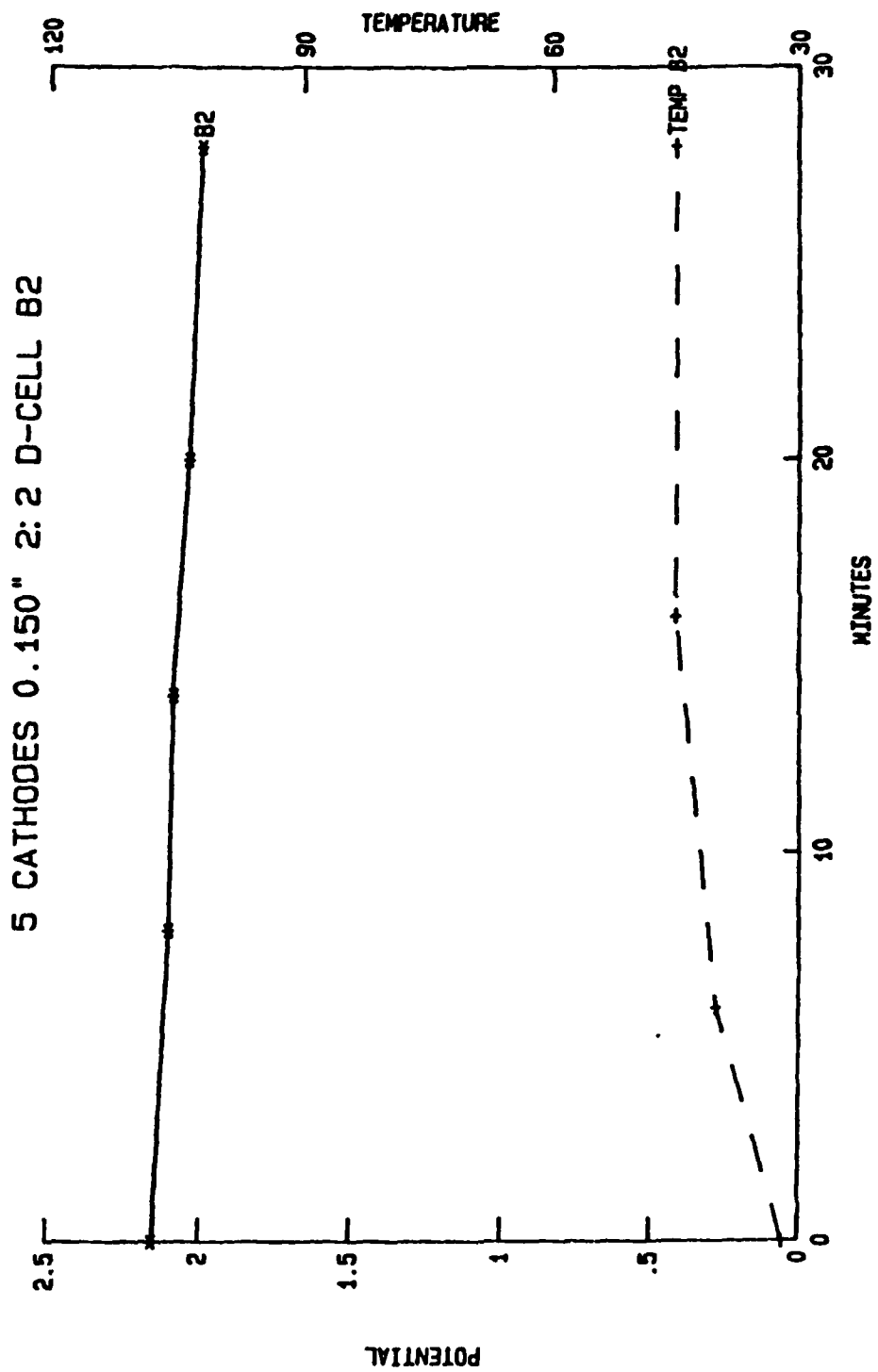


FIGURE 87 No. B2 D-Cell-Original Configuration

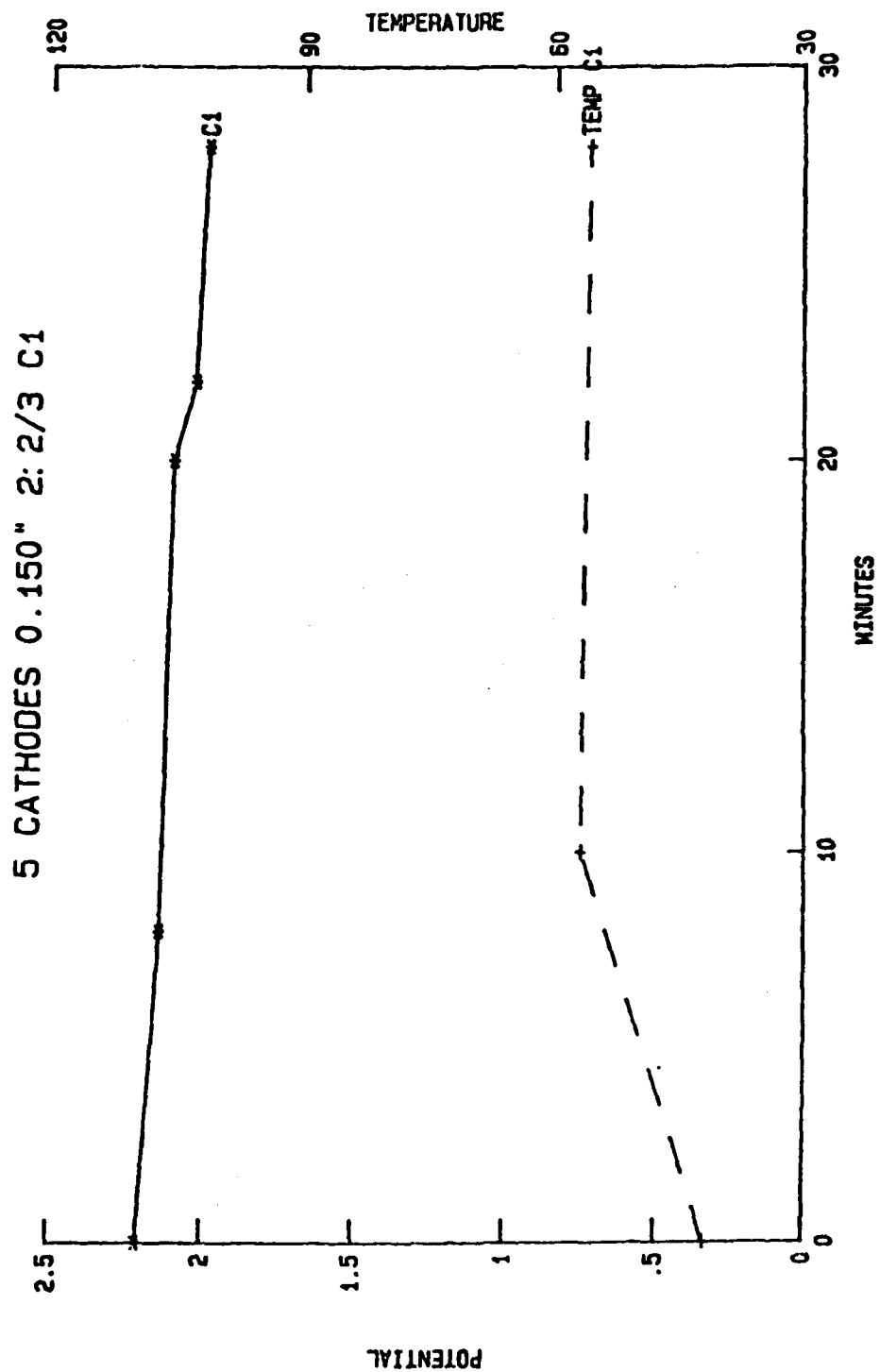


FIGURE 88 No. C1 D-Cell- Original Configuration

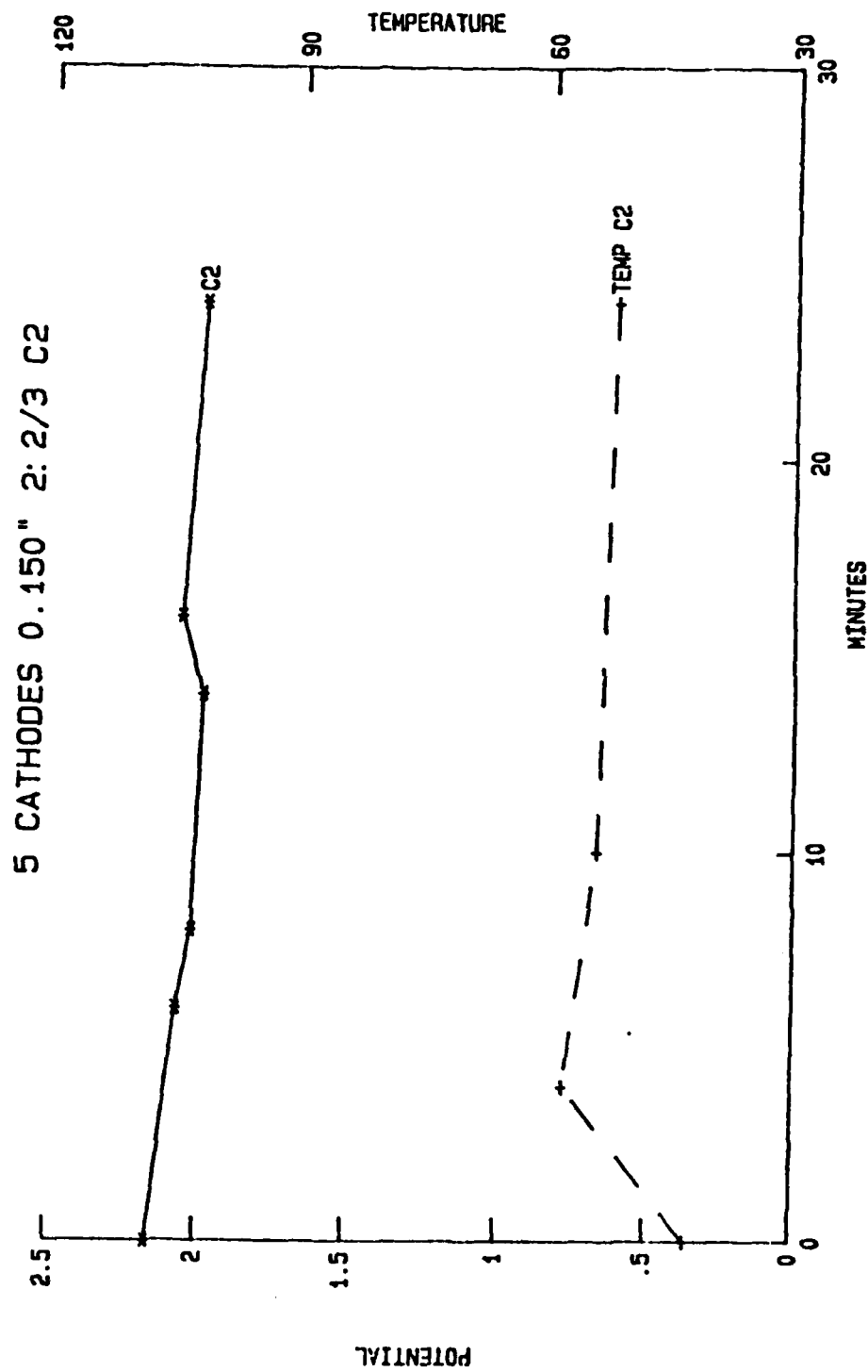


FIGURE 89 No. C2 D-Cell- Original Configuration

TABLE 58 - RECTCELL TECHNICAL DATA FOR FIGURES 90 & 91

Figure	<u>90</u>	<u>91</u>		
Discharge Min.	33	30		
\bar{V}	2.04	2.01		
VHr	0.68	0.67		
AHr	1.74	1.81	"Internal Short"	
AHr/cm ³	0.030	0.031	Cells would not carry a load!	
Watt Hr	3.55	3.64		
mA/cm ² (Avg.)	17.0	17.6		
Cat. Mix	Std	Std	Std	Std
Thickness	0.150"	0.150"	0.150"	0.150"
Quantity	5	5	5	5
Electrolyte	2:2	2:2	2:2/3	2:2/3
Avg. Ohms Load	0.39	0.37		
Temp. Max.	58C	65C		

The ohm load on these cells was manually adjusted during discharge to achieve as close as possible to a 21 minute discharge. This load variation renders comparison with other matrices difficult. However, within this matrix, it was found that the cells activated with 2M LiAlCl₄ (2:2) electrolyte could not be loaded as heavily as those activated with the 2:2/3 electrolyte. The 2:2 activated cells did hold a more stable potential at higher loading towards the end of the discharge. The larger Rectcells, though they could be loaded more heavily as a consequence of larger cathode surface area, produced capacity less than twice that of the D-cells, even with a cathode volume 2.6 times greater than the D-cells.

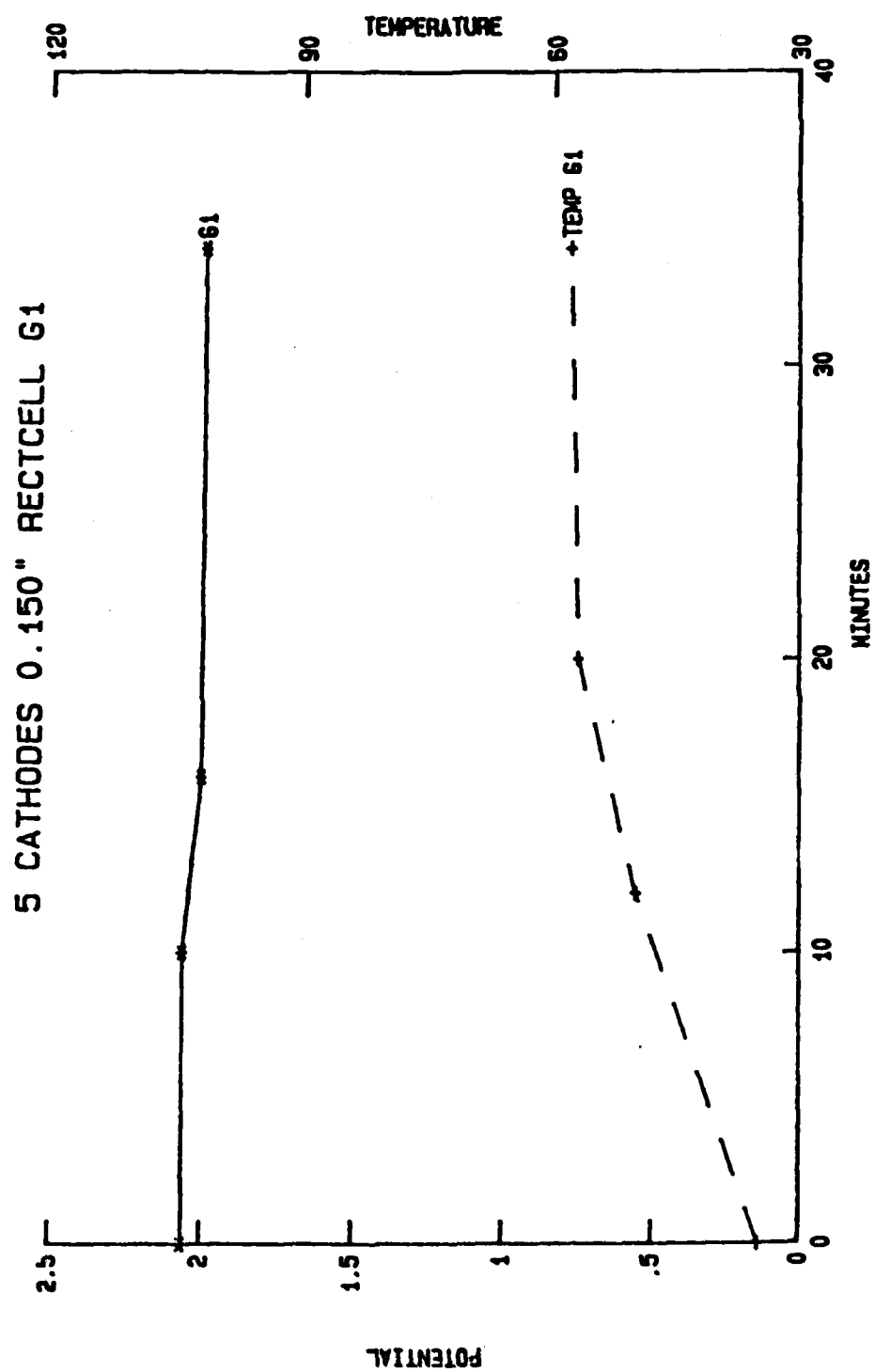


FIGURE 90 No. G1 Rectcell Scaleup

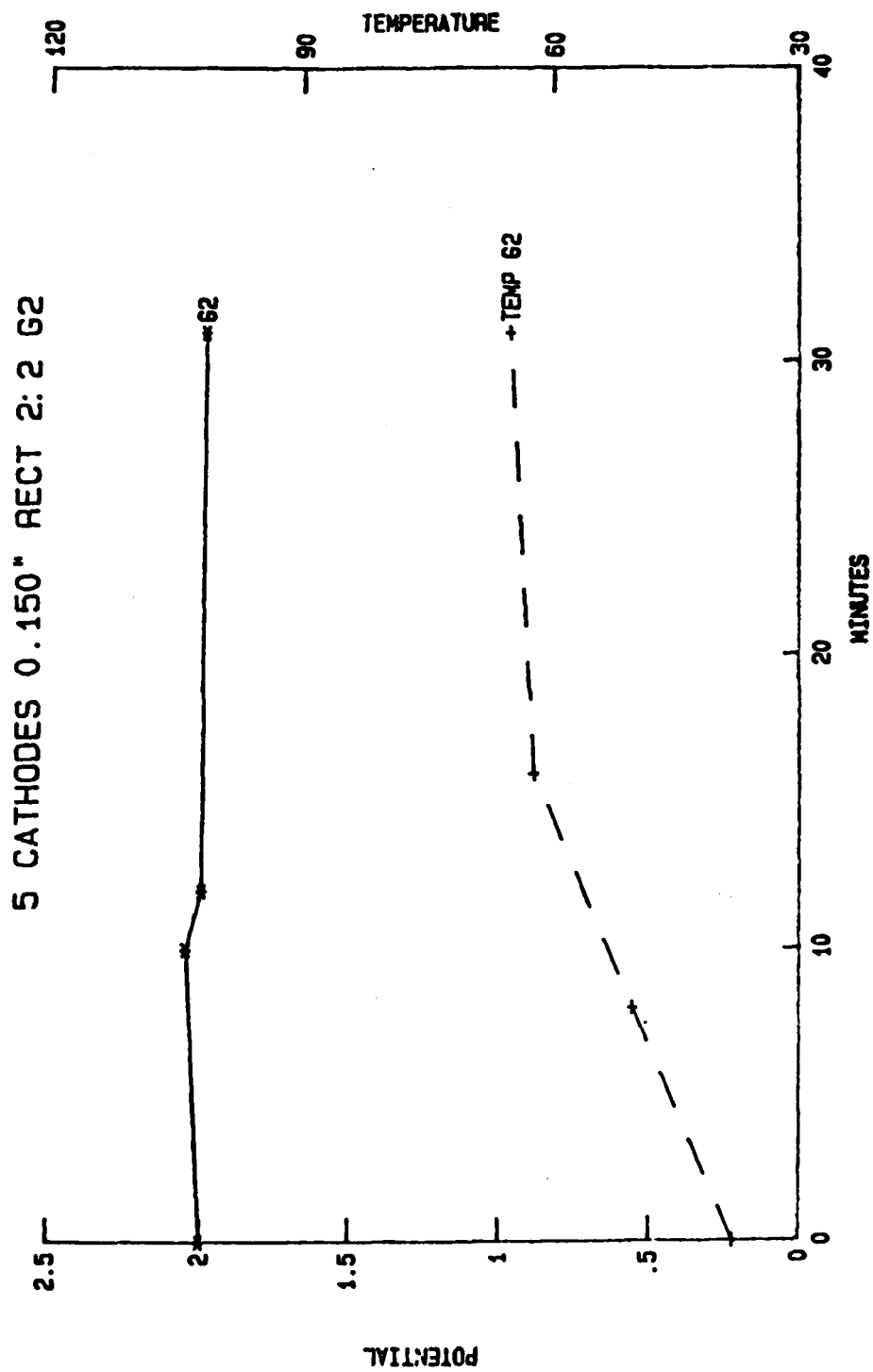


FIGURE 91 No. G2 Rectcell Scaleup

11.6 Excess Electrolyte Rectcells

Experimentation with discharged cells had indicated a possibility of electrolyte limited cells. Stainless steel cells were tested to verify the effects of extra electrolyte on cell performance. This was accomplished by fabricating a normal cell stack of 9 cathodes (1" x 1.875" x 0.050") in a 7.5 in³ Rectcell case, so that the cell stack was activated with approximately twice the normal amount of electrolyte. Likewise, 9 cathodes (1"x 1.875"x0.050") were placed in a 3.2 in³ D-cell which normally contained 15 cathodes of the same size. Two cells of each type at two electrolyte levels were discharged. 2:2 and 2:2/3 were the electrolytes used. Each cell contained 0.010" Ca Anodes with Dexter separator. Technical and Discharge data for the cells are given in Tables 59 and 60. Discharge curves are given as Figures 92-95.

TABLE 59 - EXCESS ELECTROLYTE DATA (RECTCELLS) FIGURES 92-95

<u>Figure</u>	<u>92</u>	<u>93</u>	<u>94</u>	<u>95</u>
Discharge Min.	25	20	13	11
\bar{V}	2.13	2.03	2.08	2.09
VHr	0.71	0.68	0.45	0.38
AHr	1.29	1.47	1.03	0.71
AHr/cm ³	0.093	0.106	0.074	0.051
Watt Hr	2.75	2.98	2.14	1.48
mA/cm ² (Avg.)	17.8	20.3	21.7	17.8
Cat. Mix	Std	Std	Std	Std
Thickness	0.050"	0.050"	0.050"	0.50"
Quantity	9	9	9	9
Electrolyte	2:2	2:2	2:2/3	2:2/3
Avg. Ohms Load	0.55	0.46	0.44	0.54
Temp. Max.	51C	65C	85C	96C

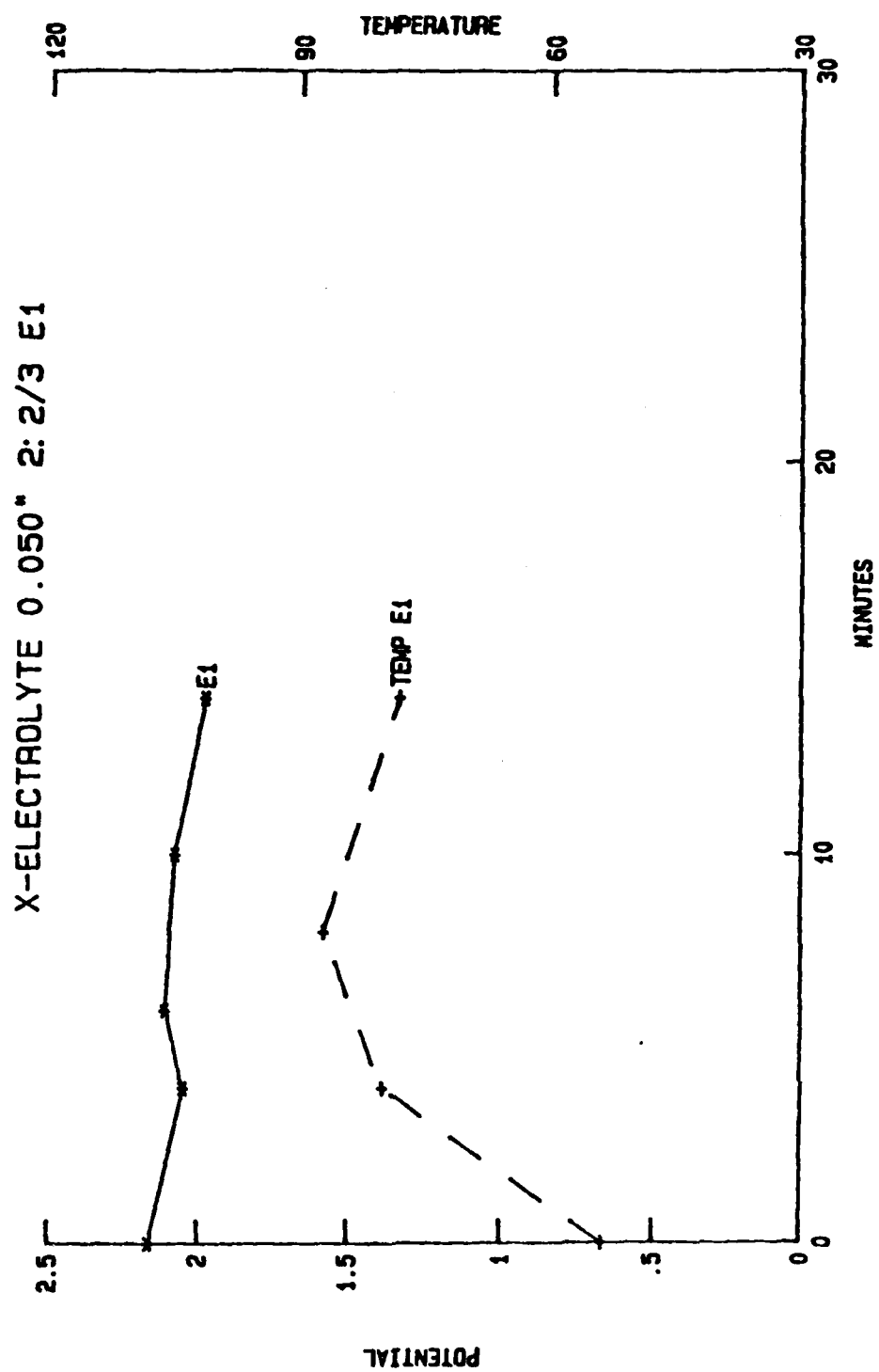


FIGURE 92 Excess Electrolyte Rectcell No. E1

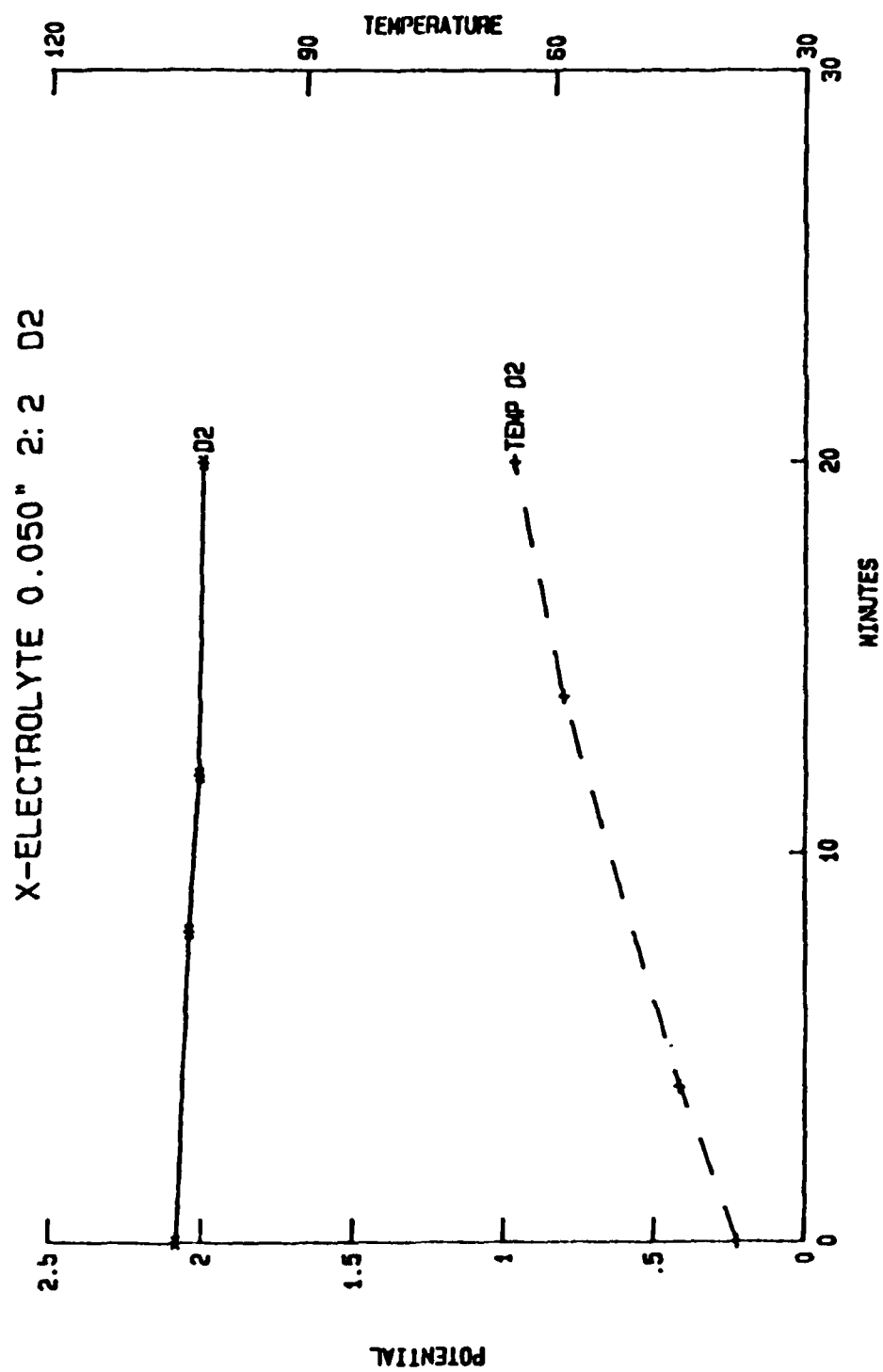


FIGURE 93 Excess Electrolyte Rectcell No. D2

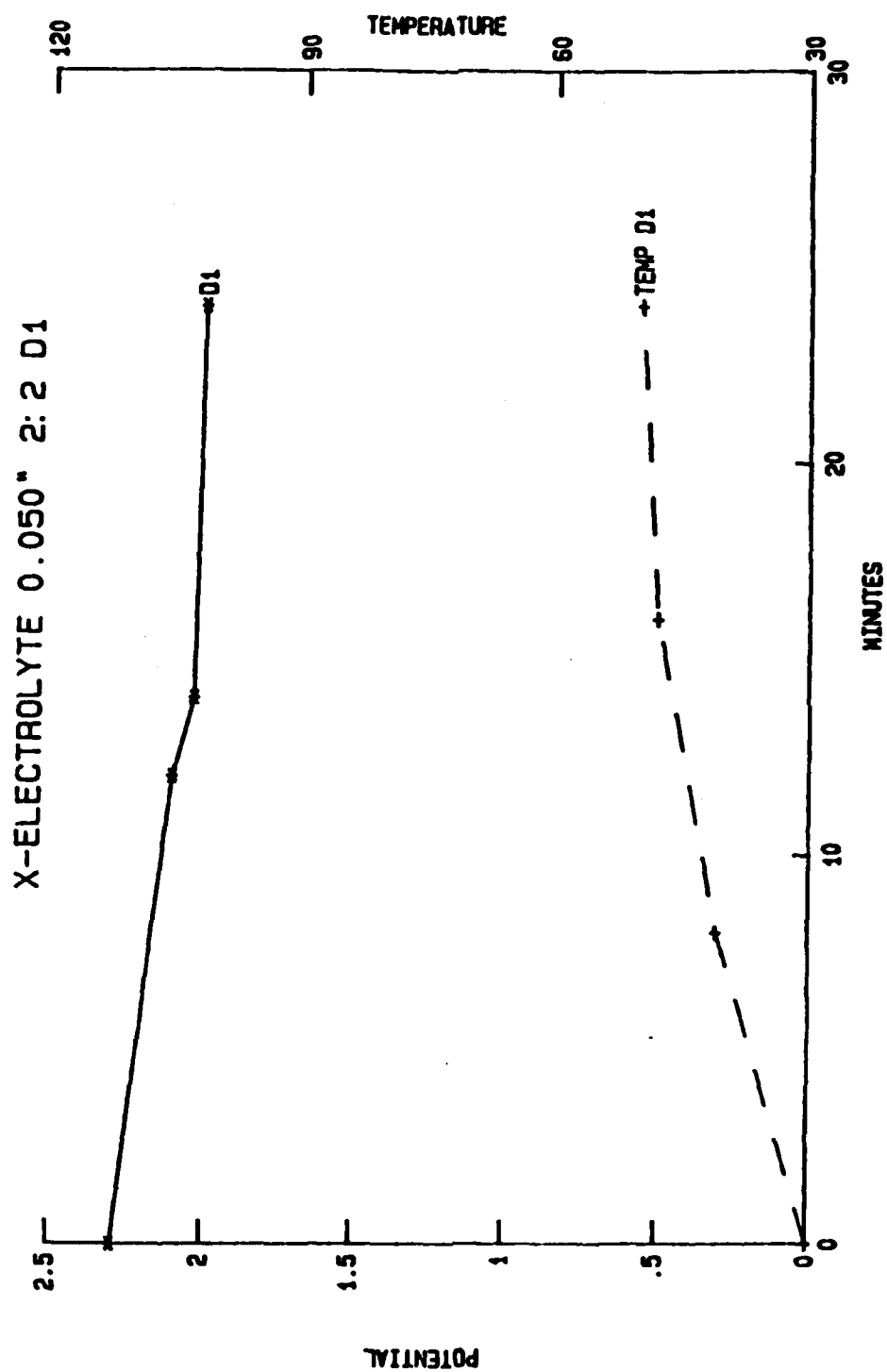


FIGURE 94 Excell Electrolyte Rectcell No. D1

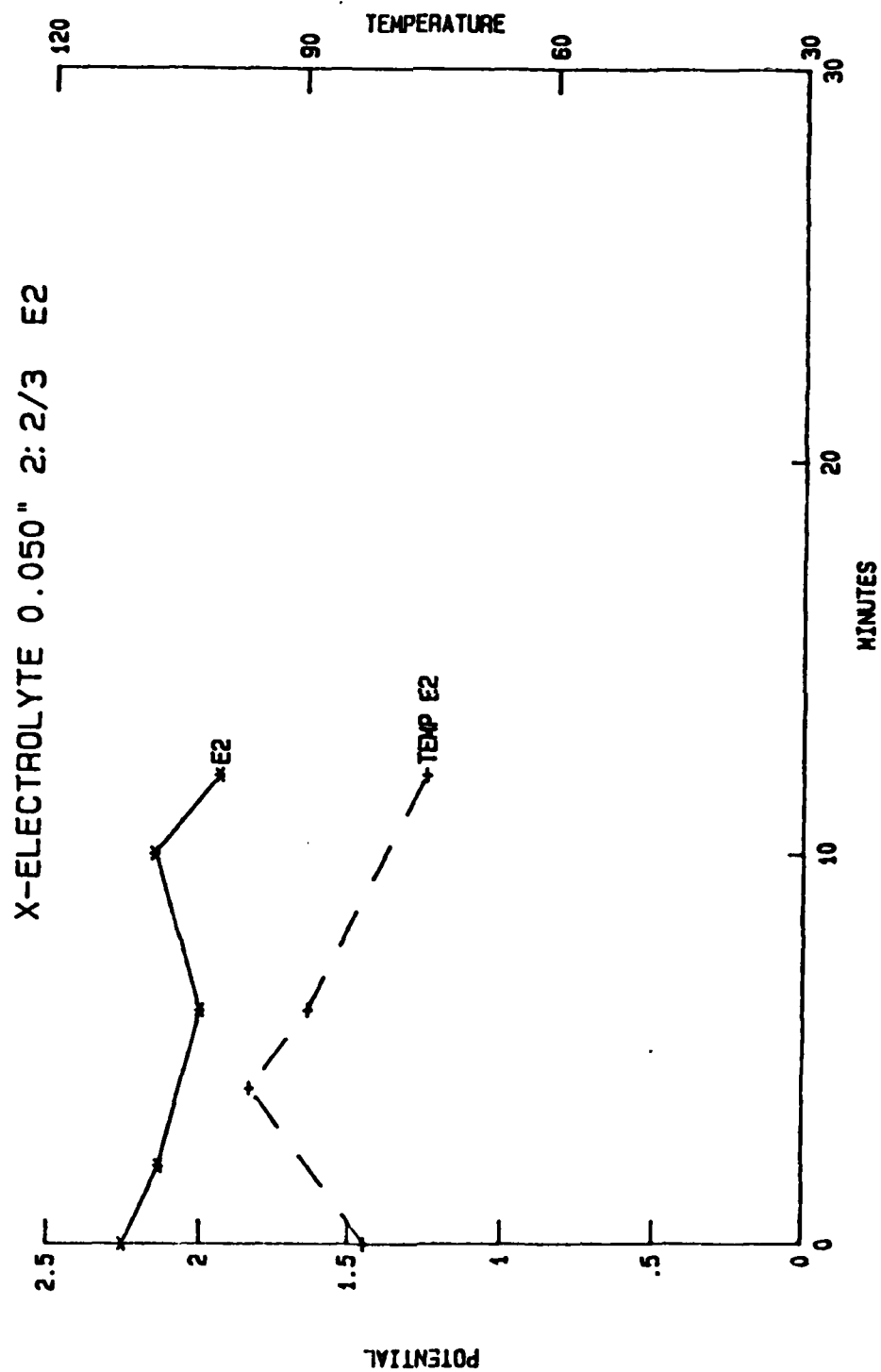


FIGURE 95 Excess Electrolyte Rectcell No. E2

TABLE 60 - EXCESS ELECTROLYTE DATA (D-CELLS) FIGURES 96-99

<u>Figure</u>	<u>96</u>	<u>97</u>	<u>98</u>	<u>99</u>
Discharge Min.	19	21	21	16
\bar{V}	2.01	2.02	2.03	2.11
VHr	0.67	0.67	0.68	0.56
AHr	1.59	1.64	1.69	1.37
AHr/cm ³	0.115	0.119	0.122	0.099
Watt Hr	3.19	3.31	3.43	2.89
mA/cm ² (Avg.)	22.0	22.6	23.3	23.6
Cat. Mix	Std	Std	Std	Std
Thickness	0.050"	0.050"	0.050"	0.050"
Quantity	9	9	9	9
Electrolyte	2:2	2:2	2:2/3	2:2/3
Avg. Ohm Load	0.42	0.41	0.40	0.41
Temp. Max.	68C	74C	83C	85C

Results from all cells indicated failure to achieve the performance level of cells with a full stack. The Rectcells in particular, performed quite poorly compared to D-cells with the same cell stack. The D-cells, however, came close to equalling the performance of their fully stacked counterparts, indicating the extra electrolyte, or the looser cell stack, or a combination of both conditions, allowed enhanced performance. The D-cells were loaded at an average 0.4-ohm load, as were most of the previous cell series. This placed a higher mA/cm² loading on the D-cell cathodes, without markedly decreasing overall performance.

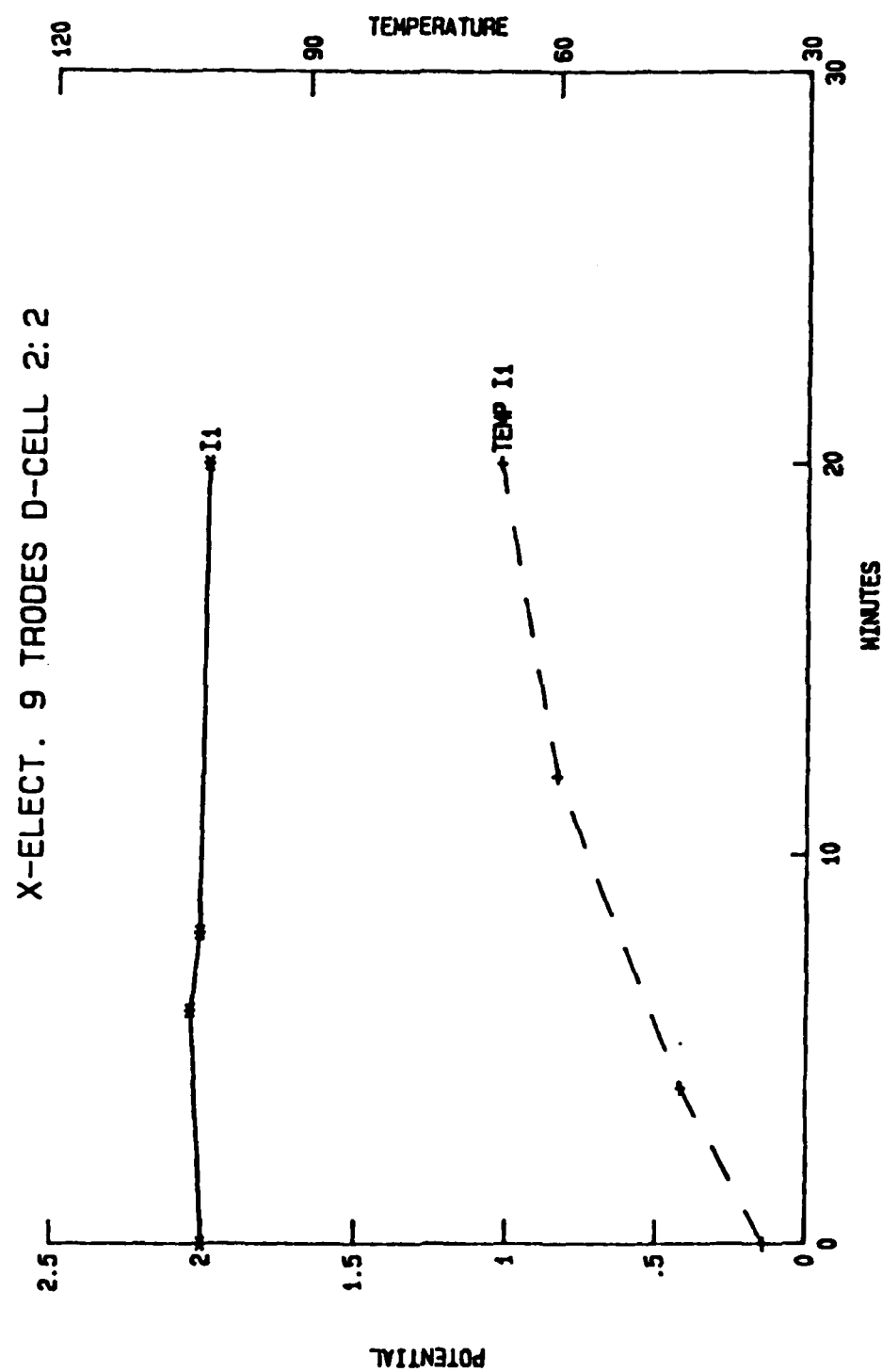


FIGURE 96 Excess Electrolyte D-Cell No. 1

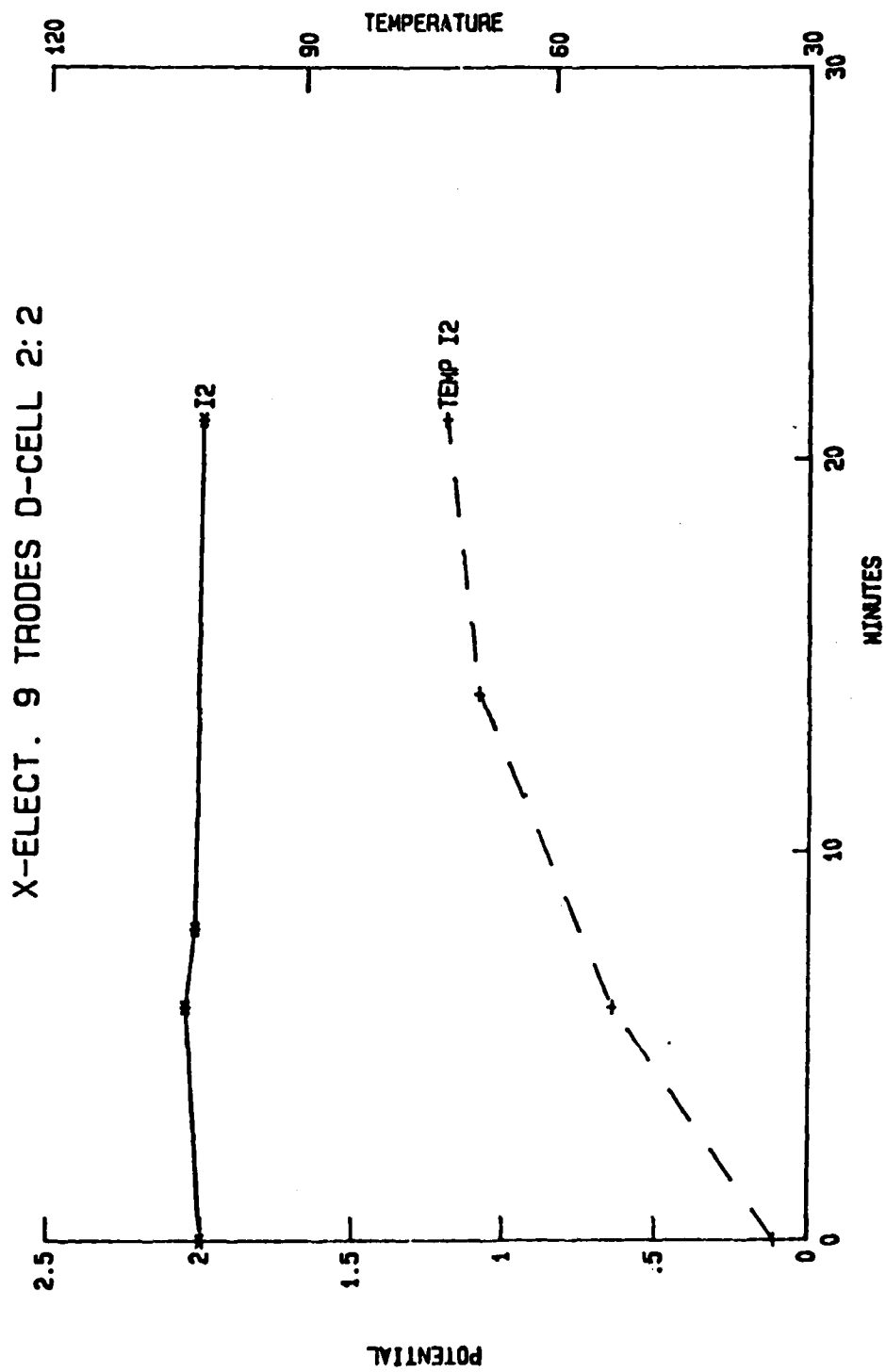


FIGURE 97 Excell Electrolyte D-Cell No. 2

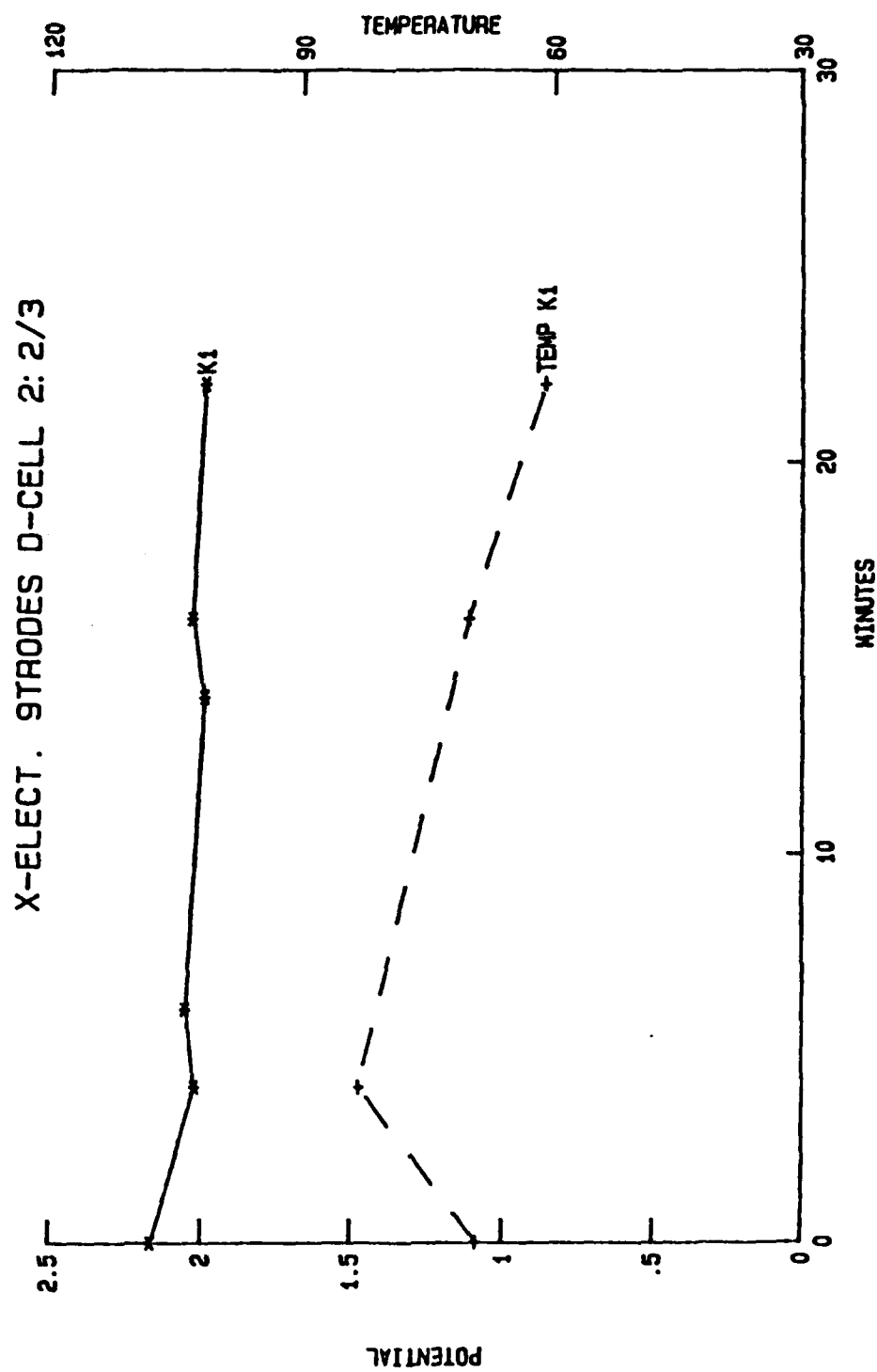


FIGURE 98 Excess Electrolyte D-Cell No. 3

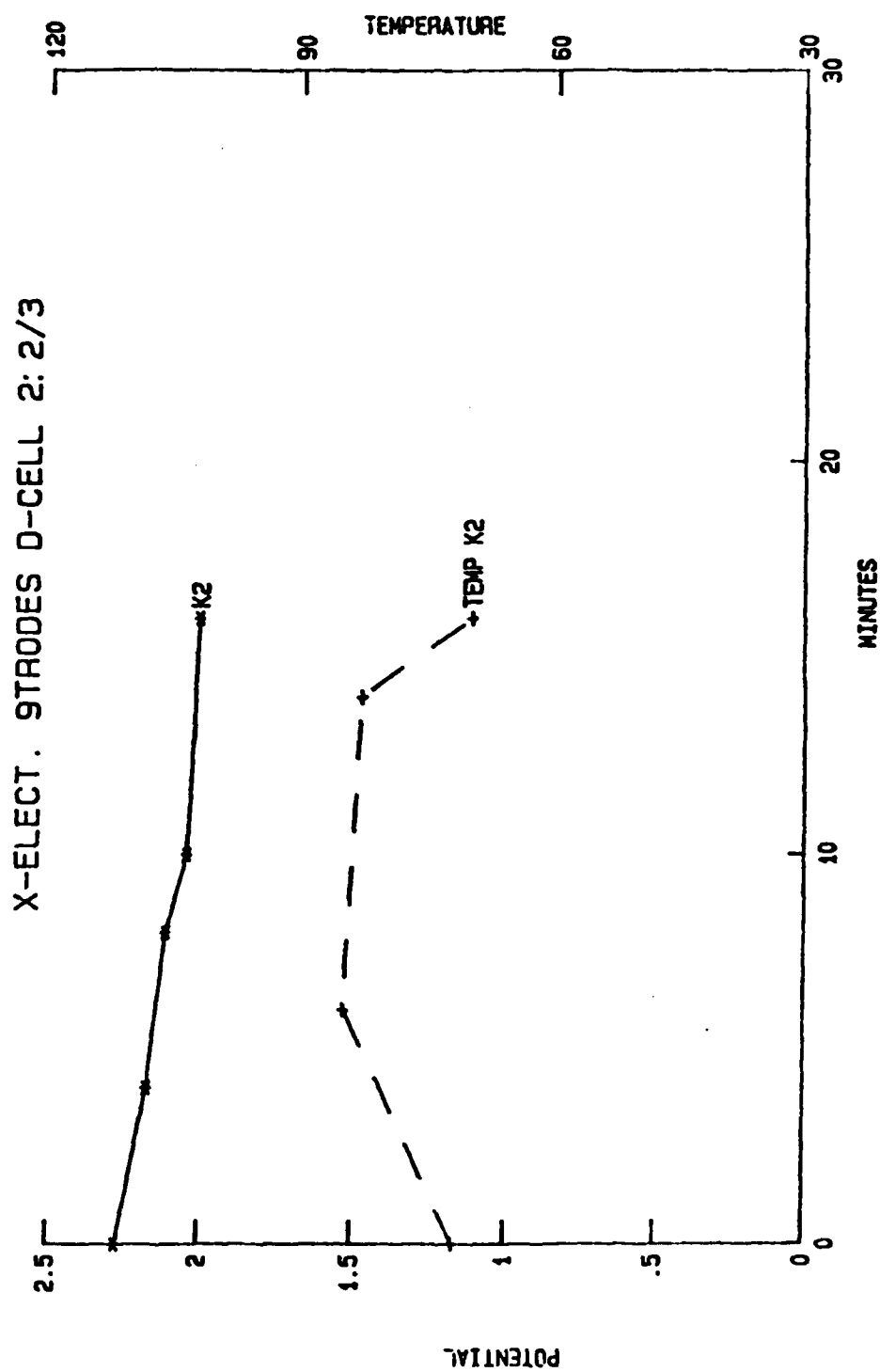


FIGURE 99 Excess Electrolyte D-Cell No. 4

11.7 Prototype Battery Attempt

A prototype battery was constructed. It consisted of a Plexiglas^(R) casing, rectangular, 3" x 3" x 9" high overall. Plexiglas^(R) dividers separated the interior into 15 cells. A header, also made of plastic, incorporating the cover from a stainless steel cell, was attached. Cell components consisted of five cathodes and six anodes, 2.5" x 8.0" x .010", with .006" Manning separator. The cells were connected in series. Attempts to activate the cell were unavailing, due to seam leakage preventing a vacuum being drawn on the cell.

A second prototype battery was constructed. Also of plastic, this casing consisted of 16 cell compartments, fed with electrolyte from below from a reservoir compartment, while a vacuum was drawn from the top of the casing. Cell components consisted of 5 cathodes and 6 anodes, separated by .006 Manning separator, the cathodes measuring 2.0" x 2.375" x .020", with anodes measuring 2.0" x 2.376" x .010". The overall battery case measured 6.5" x 2.5" x 3.5" cells were connected in series. The battery was vacuum activated with approximately 300 ml of 2:1 electrolyte. Intense cell bubbling was noted immediately upon activation. The battery remained on open circuit for 5-10 minutes with an expected 53 volts. Seconds after load was applied the battery exploded. Examination of the debris revealed the 150 psi vent in the cell header to be intact, indicating the .125 inch cell casing gave way.

Bag cells were used to investigate the bubbling reaction. Each bag cell consisted of two Ca anodes .010 thick, Manning separator, and one cathode measuring 1.5" x 2.25" x .020". Four of these bag cells were connected in series and discharged. Data for two trials at different loads are given on the next page.

	<u>Trial I</u>	<u>Trial II</u>
OCV	12.77	12.40
Cat. Quality	4	4
Cat./Cell	1	1
Cell Quantity	4	4
Electrolyte	2:1	2:1
\bar{V}	10.35	8.61
\bar{A}	0.28	0.91
$\bar{\Omega}$	37.0	9.46
V Hr	6.04	1.89
A Hr	0.16	0.20
Watt Hr	1.68	1.72
mA/Cm ²	6.4	21
Discharge (Min.)	35	13
Max. Temp.	60C	60C

Intense bubbling and gassing was noted with the load connected. The gassing subsided when the load was disconnected. The 60C temperature attained during discharge is considerably less than the boiling point of Thionyl Chloride. The gassing, therefore, is a reaction of the Ca/SOCl₂ system.

Difficulty with multi-cell, stack cell configurations housed in the same battery case prompted investigations into two cell systems.

A stainless steel Rectcell (7.5 in³) containing two cells in series, was discharged with data listed in Table 61 and discharge curve given in Figure 100.

TABLE 61 - TWO-CELL BATTERY

Cell Quantity	2
Cathodes/Cell	5
Total Cathodes	10
Cathode Size	1.562" x 1.750" x 0.020"
Ca Anode Size	0.010" thick
Electrolyte	2:1 60 ml
OCV	6.63
\bar{V}	6.63
Load (Ohm)	1.25
V Hr	1.35
A Hr	1.08
Watt Hr	5.65
A Hr/Cm ³	0.12
mA/Cm ²	21
Discharge Time (Min.)	18

Gassing of the cell while on open circuit was minimal, however, intense bubbling of the electrolyte was noted during discharge. An IR Scan of the gas appears in Figure 101. For comparison an IR scan of 2:1 lab prepared electrolyte fumes appear in Figure 102.

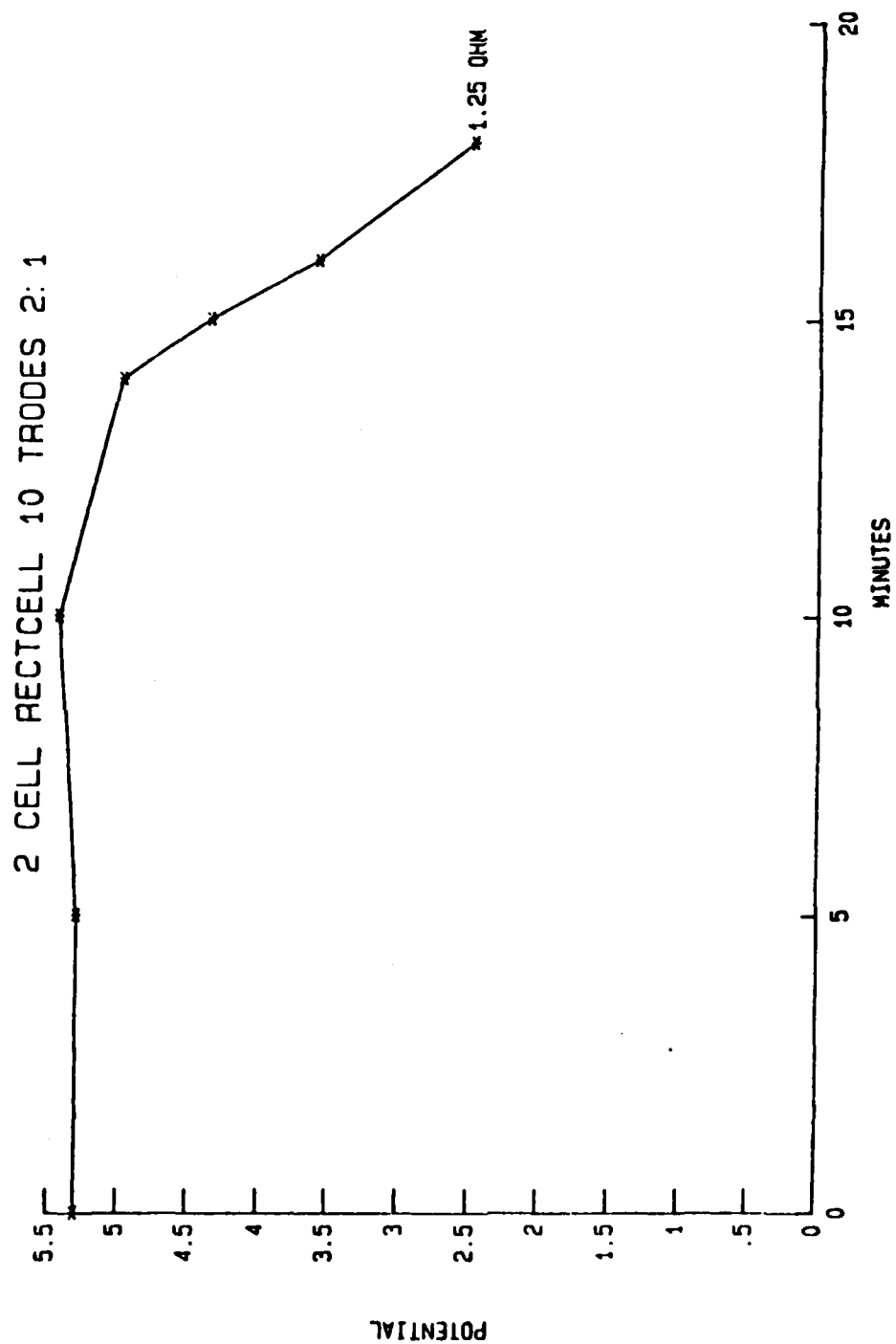


FIGURE 100 Two Cell Rectcell Discharge

SPECTRUM NO. 7
 DATE 8/21/64
 SAMPLE rect cell
discharge gas products
 SOURCE rect cell
 STRUCTURE _____
 PATH 1 mm SiO₂
 SOLVENT none
 CONCENTRATION _____
 PHASE gas
 COMMENTS See Ref
 ANALYST C.T.

INFRARED
SPECTROPHOTOMETER

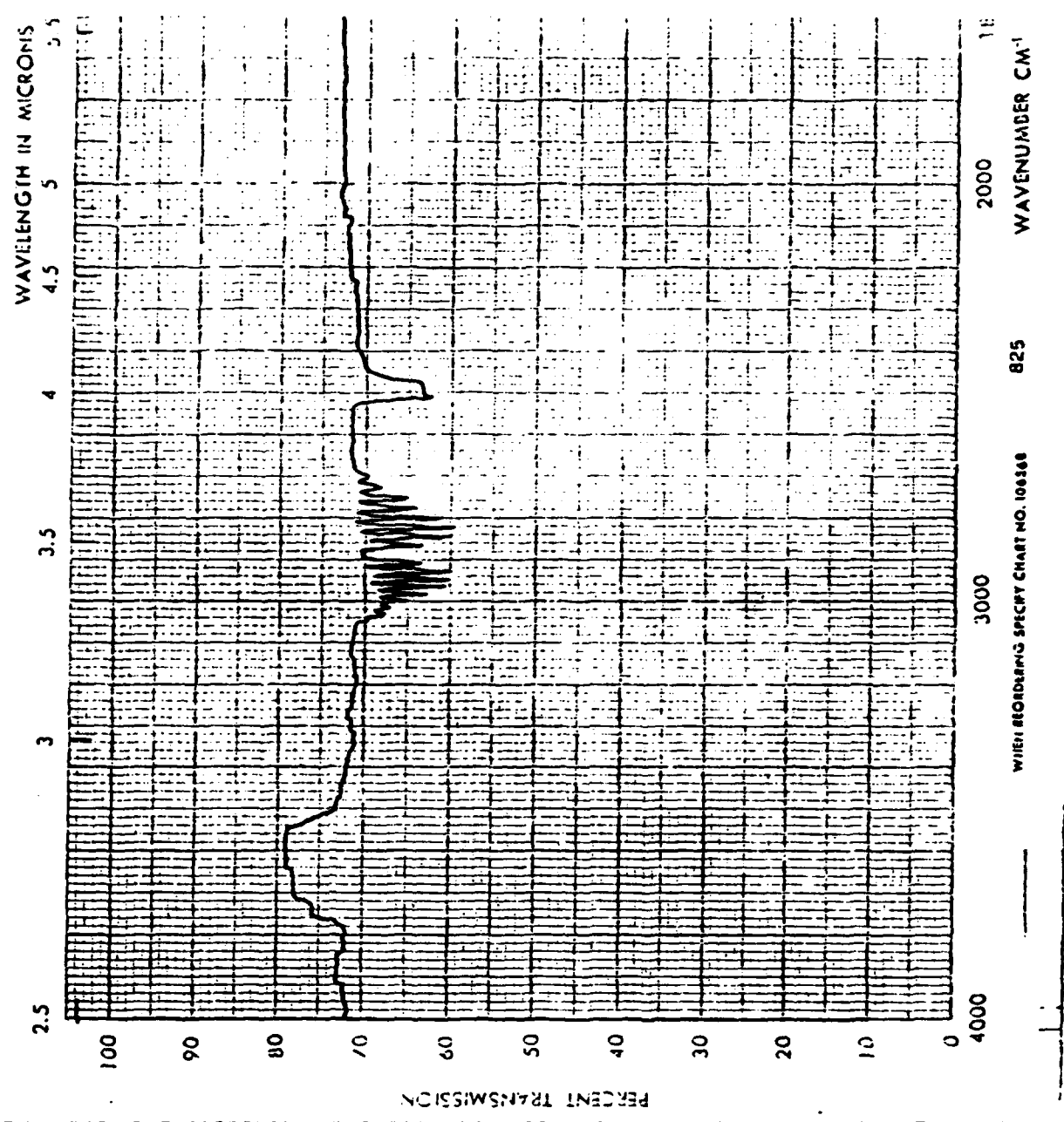


FIGURE 101 IR Scan - Rectcell Discharge Gas Products

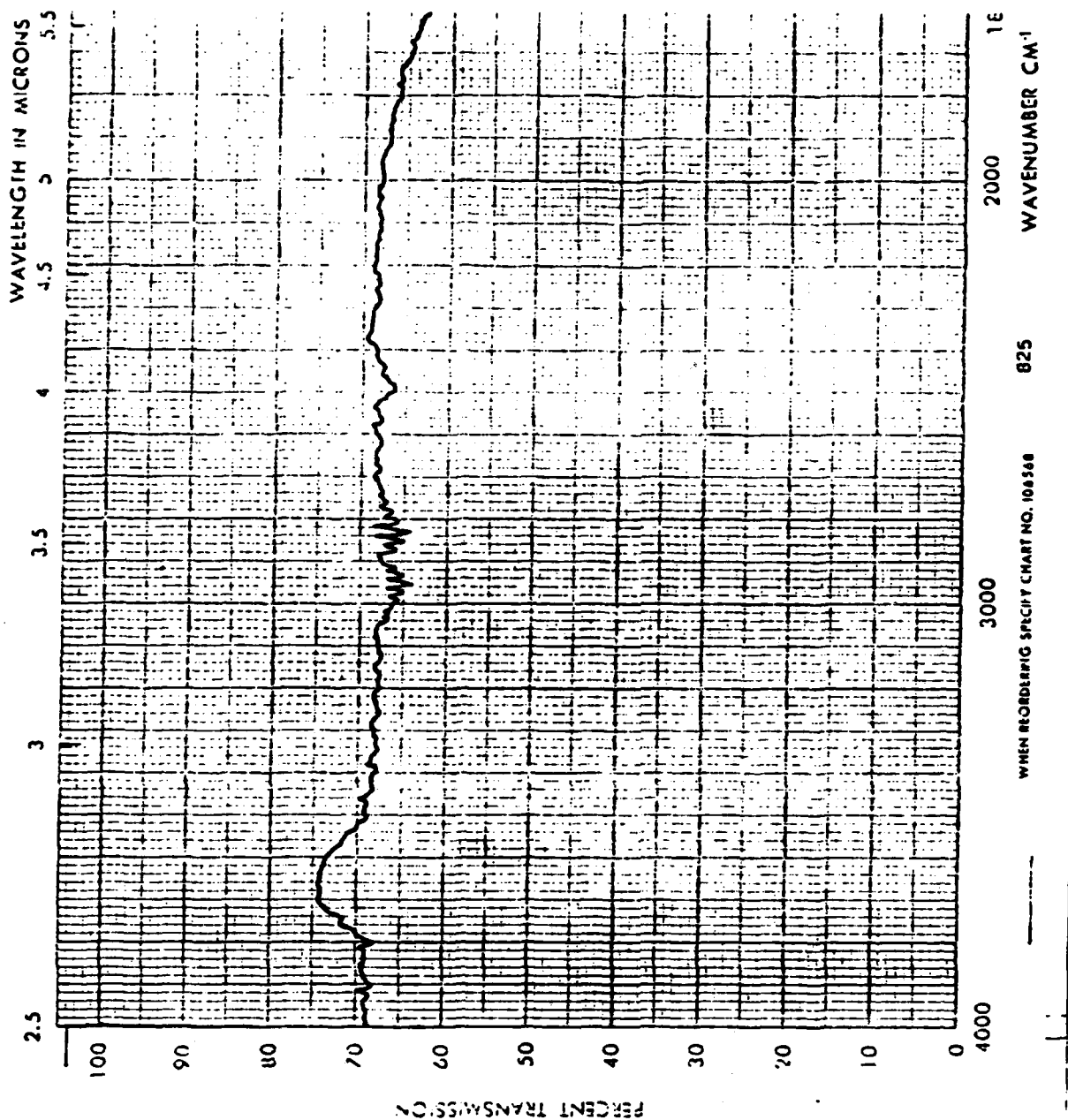


FIGURE 102 IR Scan - Lab 2:2 Electrolyte Vapor

INFRARED
SPECTROPHOTOMETER

SPECTRUM NO. 5

DATE 2/29/51

SAMPLE Electrolyte vapor

SOURCE Lab

STRUCTURE 502

PATH 1 mm

SOLVENT None

CONCENTRATION ---

PHASE ---

COMMENTS 1. 2. 3.

ANALYST ---

11.8 Open Battery Experiment

Two experimental reserve cell batteries were assembled utilizing plastic cell cases with plastic dividers between cells. The overall configuration contained 1 cathode and 2 calcium anodes per cell for a total of 15 cells. Cells were connected in series. The cell cases were open to the atmosphere. Intense electrolyte bubbling caused loss of electrolyte, possibly shortening the discharge prematurely. Discharge data is tabulated in Table 62 below, and discharge curves are given in Figures 103 and 104. All calculations are based on 20 minutes discharge, however, the cells actually ran longer.

TABLE 62 - OPEN BATTERY DATA 103-104

	<u>Trial #1</u>	<u>Trial #2</u>
Cell Quantity	15	15
Cathodes/Cell	1	1
Total Cathodes	15	15
Cathode Size	1"x1.875"x0.050"	1"x1.875"x0.050"
Anode Size	0.010" thick	0.010" thick
Electrolyte	2:1 100 ml	2:1 100 ml
OCV	49.5	49.1
\bar{V}	41.4	42.4
Load (Ohm)	109	105
V Hr	13.82	14.12
A Hr	0.13	0.13
Watt Hr	5.26	5.70
A Hr/cm ³	0.0056	0.0056
mA/cm ²	1.0	1.3
Discharge Time (Minutes)	23	36

#1 15 CELL 15 CATHODE 2:1 22C

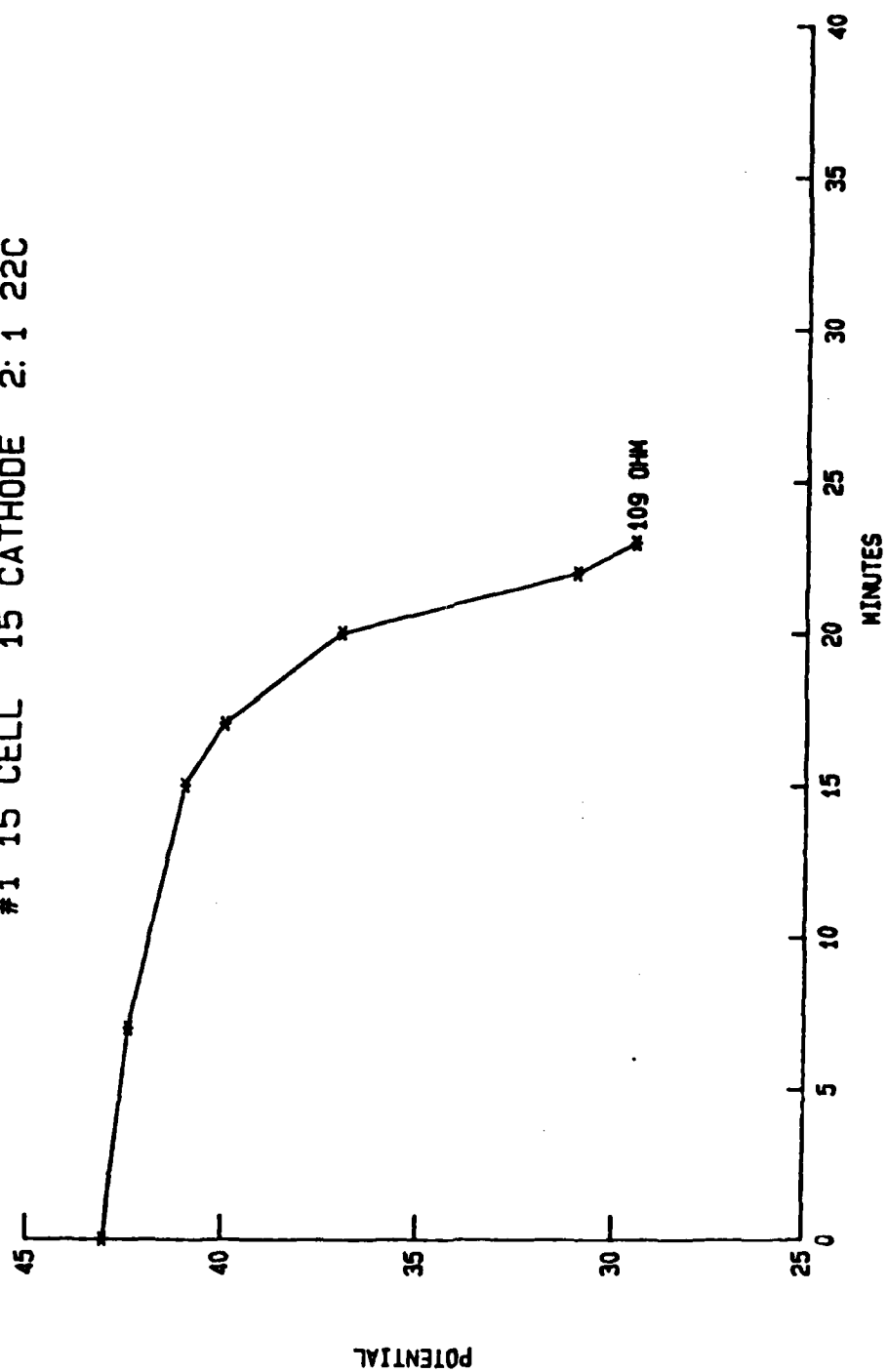


FIGURE 103 Trial One - Open Battery

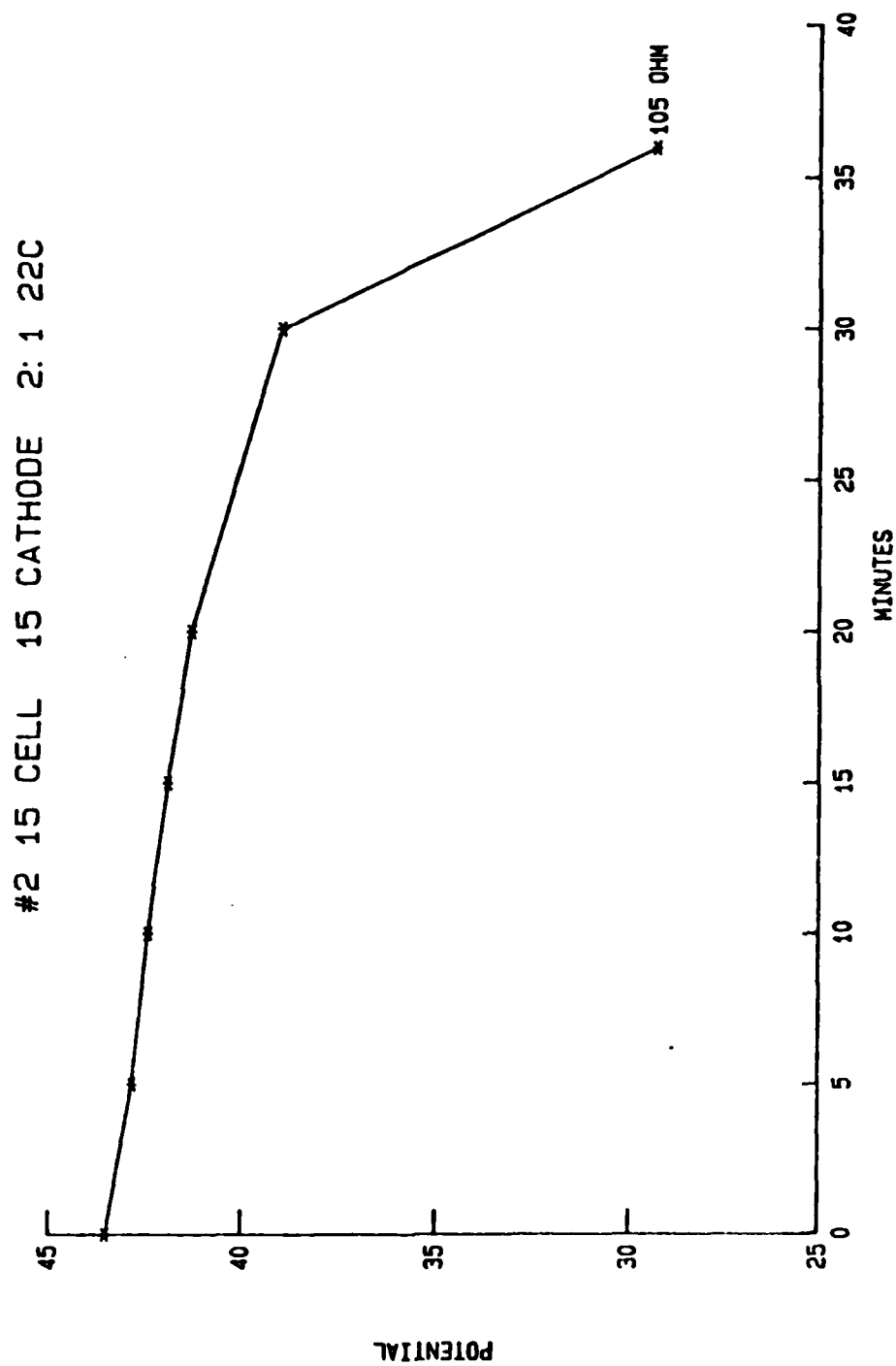


FIGURE 104 Trial Two-Open Battery

The cells were discharged to a cut-off voltage of 2.0 volts. Current density on discharge was a disappointing 1.0 and 1.3 mA/cm², respectively. Current density needs to be in the 20-30 mA/cm² range for the desired reserve battery.

Experimental Cell #3 was discharged utilizing a battery case open to the atmosphere to relieve gas pressure but designed to contain the electrolyte. The design worked adequately but the performance was comparable to the two previous batteries. The battery contained 4 cells/battery, 4 cathodes/cell, cathode size 2" x 2" x 0.015", cells connected in series for a 13.5 OCV.

Experimental Cell #4 was assembled identically to Cell #3 except each cell of the battery was isolated. This was done to observe the effects on the gassing problem. Gassing and performance was comparable to the three previous cells.

SECTION XII

FOURTH PHASE RESERVE CELL WORK

12.1 Cathode Thickness/Carbon/Preparation Matrix

A matrix of glass test cells was set up to compare Black Pearls 2000 carbon, made by Cabot Corp., with the standard Shawinigan 50% compressed that had been utilized in cathodes to this point. It was thought the comparatively high surface area Cabot carbon might resist discharge product plugging more successfully than the Shawinigan carbon. Also tested was the performance of the cathodes versus thickness with two different cathode fabrication techniques. The standard cathode fabrication technique to this point had been to blend dry TFE powder with the carbon, then press the cathode in a die, then sinter the pressed cathode at 620°F for 20 minutes to flow the teflon. This technique is referred to as pressed/baked. The alternate technique being evaluated consists of suspending the carbon in water, adding the TFE as TFE-30 suspension, blending, then vacuum filtering the mix to form half a plate. The process is repeated to form the second half of the plate, then the half plates are "sandwiched" with collector grid already tabbed with nickel tab material. The plate is then pressed twice at low (250 psi) pressure between blotter paper, then at high (2500 psi) pressure. A stack of plates is then made up, interleaved with aluminum foil, and tightly jigged between aluminum plates and allowed to air dry for 24 hours. The jigged stack is then sintered at 620°F for 20 minutes. After separation of the plates, they are placed in a vacuum oven at 165°F for a final 72 hour drying period. The plates are then cut to final size. This technique is referred to as pasted/baked.

Data from the glass test cell matrix is given in Table 63. Using the matrix utilization results (Ahr/cm³) for comparison, and the trial A results as a baseline, the cathodes fabricated with pasted/baked technique far outperformed the pressed/baked cathodes. In this limited matrix, the trial 15%

TFE, pasted/baked cathodes performed best of those made with Shawinigan carbon. The Trial H and J Black Pearls cathodes slightly outperformed the best Shawinigan cathodes.

12.2 Cathode Thickness/Carbon/Binder Matrix

A second matrix of glass test cell was set up to evaluate cathode performance under typical reserve cell configurations (2:1 $\text{AlCl}_3/\text{LiCl}$ electrolyte, 25 ohm load) Ketjenblack carbon, a product of Noury Corp., was added to the carbon evaluation. In relative surface area, it lay between the Shawinigan carbon and the Cabot Black Pearls 2000. Literature reports had indicated good initial success in lithium/thionyl chloride cells using carbon for cathodes construction that had been washed with acetone. This technique was evaluated for the calcium/thionyl chloride cell in this matrix.

Shawinigan carbon was stirred overnight in acetone, then filtered on a Buchner funnel with further clean acetone rinses, followed by distilled water rinses to remove the acetone.

Results of the matrix are given in Table 64. Using the matrix utilization figures (Ahr/cm^3) for comparison, the Ketjenblack carbon did not perform as well as either of the other carbons and was dropped from further testing with 2:1 electrolyte. The acetone-washed Shawinigan carbon did not perform nearly as well as the unwashed in any configuration. Black Pearls 2000 carbon cathodes with 4% binder content did not perform as well as either the same configuration electrode with either 7.5 or 15% TFE content.

TABLE 63 - CATHODE THICKNESS/CARBON/PREPARATION MATRIX

ALL CELLS DISCHARGED WITH 2:1 AlCl_3 : LiCl ELECTROLYTE AND 25 OHM LOAD

	<u>TRIAL DISCHARGE</u>	<u>CATHODE MATERIAL</u>	<u>SIZE (INCHES)</u>	<u>DISCHARGE TIME (MIN.)</u>	<u>OCV</u>	<u>\bar{V}</u>	<u>A-Hr</u>	<u>A-Hr/ CM^3</u>
A	1	Shaw, 10% Pressed	.045x.690 x .540	21	3.37	2.35	0.033	0.120
	2	Baked		29	3.38	2.37	0.046	0.167
B	1	Blk. Prls. 2000 10% Pressed Baked	.045x.690 x .540	34.5	3.23	2.43	0.056	0.204
C	1	25% 2000 +75% Shaw Pressed 10% Baked	.045x.690 x .540	19.25	3.29	2.37	0.030	0.109
	2			20	3.24	2.38	0.032	0.116
D	1	Shaw 7.5% Pasted/ Baked	.018x.700 x.690	17	3.35	2.25	0.025	0.225
	2		.018x.690 x .540	15	3.38	2.21	0.022	0.200
E	1	Shaw 7.5% Pasted/ Baked	.030x.695 x.540	37	3.29	2.29	0.056	0.304
	2		.030x.675 x.535	17	3.33	2.29	0.26	0.147
F	1	Shaw 15% Pasted/ Baked	.014x.690 x .540	20.5	3.38	2.26	0.031	0.365
	2		.013x.690 x .540	20	3.38	2.24	0.030	0.380
G	1	Shaw 15% Pasted/ Baked	.025x.695	26.5	3.36	2.28	0.040	0.260
	2		.025x.700 x .540	22	3.37	2.24	0.033	0.213

TABLE 63 - continued

<u>TRIAL</u> <u>DISCHARGE</u>	<u>CATHODE</u> <u>MATERIAL</u>	<u>SIZE</u> <u>(INCHES)</u>	<u>DISCHARGE</u> <u>TIME (MIN.)</u>	<u>OCV</u>	<u>-</u> <u>V</u>	<u>A-Hr</u>	<u>A-Hr/</u> <u>CM³</u>
H	1	Blk Prl	24.5	3.35	2.42	0.040	0.667
	2	2000 7.5% Pasted/ Baked	x .530 12.5 x .535	3.11	2.35	0.020	0.333
I	1	Blk. Prl	22.5	3.30	2.48	0.040	0.317
	2	2000 7.5% Pasted/ Baked	x .550 11.5 x .545	3.23	2.37	0.018	0.146
J	1	Blk Prl	19.5	3.28	2.33	0.030	0.411
	2	2000 15% Pasted/ Baked	x .540 17.5 x .540	3.26	2.40	0.028	0.384
K	1	Blk Prl	16.5	3.26	2.51	0.028	0.200
	2	2000 15% Pasted/ Baked	x .560 15.5 x .670	3.25	2.44	0.025	0.172

TABLE 64 - CATHODE THICKNESS/CARBON/BINDER MATRIX

ALL CELLS DISCHARGED WITH 2:1 AlCl_3 :LiCl ELECTROLYTE AND 25 OHM LOAD

TRIAL DISCHARGE	CATHODE MATERIAL	SIZE (INCHES)	DISCHARGE TIME (MIN.) ABOVE 2.0V	OCV	\bar{V}	A-Hr	A-Hr/ CM^3
I	1 Shawinigan Acetone Washed	.012"x.700" x.535"	7½	3.30	2.20	0.011	0.149
	2 7.5% Pasted/ Baked	.013"x.690" x.540"	12	3.22	2.27	0.018	0.228
II	1 Shawinigan Acetone Washed	.027"x.695" x.540"	20½	3.30	2.31	0.032	0.193
	2 7.5% Pasted/ Baked	.027x.700" x .540"	17½	3.28	2.24	0.026	0.156
III	1 Shawinigan Acetone Washed	.017x.690 x .550	17	3.36	2.32	0.026	0.245
	2 15% Pasted/ Baked	.015x.690 x.550	2/3	3.33	2.10	0.001	0.011
IV	1 Shawinigan Acetone Washed	.030x.695 x .545	22	3.36	2.30	0.034	0.183
	2 15% Pasted/ Baked	.030x.695 x .540	18	3.37	2.19	0.026	0.141
V	1 Shawinigan Acetone Washed	.045x.690 x .540	14	3.26	2.33	0.022	0.080
	2 10% Pressed/ Baked	.045x.690 x .540	16	3.29	2.33	0.025	0.091
VI	1 Blk. Prls 4% TFE	.690x.540 x .012	12¼	3.28	2.47	0.020	0.281
	2 Pasted/ Baked	.690x.540 x .012	14	3.26	2.41	0.022	0.308
VII	1 Ketjenblack 7.5% TFE	.690x.540 x .015	18	3.29	2.46	0.030	0.321
	2 Pasted/ Baked	.690x.540 x.015	14½	3.26	2.39	0.023	0.252

TABLE 64 - continued

<u>TRIAL DISCHARGE</u>	<u>CATHODE MATERIAL</u>	<u>SIZE (INCHES)</u>	<u>DISCHARGE TIME (MIN.) ABOVE 2.0V</u>	<u>OCV</u>	<u>\bar{V}</u>	<u>A-Hr</u>	<u>A-Hr/ CM³</u>
VIII	1 Ketjenblack 7.5% TFE	.700x.520 x.028	25	3.28	2.48	0.041	0.247
	2 Pasted/ Baked	.695x.540 x.025	19	3.26	2.40	0.030	0.195
IX	1 Ketjenblack 15% TFE	.690x.550 x.015	19	3.29	2.45	0.031	0.333
	2 Pasted/ Baked	.690x.550 x.015	16	3.26	2.37	0.025	0.272
X	1 Ketjenblack 15% TFE	.690x.540 x.025	24-3/4	3.29	2.47	0.041	0.266
	2 Pasted/ Baked	.690x.540 x.025	25	3.29	2.40	0.040	0.262
XI	1 Acetoned Shawinigan	.700x.540 x.050	33	3.37	2.30	0.051	0.163
	2 Pasted/ Baked	.690x.545 x.042	36	3.33	2.32	0.056	0.215

12.3 Balanced Electrolyte Matrix

A matrix of glass test cells was constructed and discharged using high but balanced salt electrolytes. Concentrations evaluated were 2:2, 3:3 and 4:4 mole ratio of AlCl_3 to LiCl . Results from the glass cell matrix are given in Table 65.

At the approximately 20 ma/cm^2 rate considered practical for the high rate reserve cell desired, none of the carbons tested produced as high a utilization rate with 2:2 electrolyte as had been produced with 2:1 electrolyte. Surprisingly, Ketjenblack carbon at a 7.5% TFE level, which had the worst performance with 2:1 electrolyte, performed the best with 2:2 electrolyte, producing an average .34 Ahr/cm^3 . The 3:3 and 4:4 electrolytes produced extremely poor performance and were dropped from further testing.

12.4 D-Cell Matrix

Five D-cells were constructed. Three used nominal .012" thick cathodes of 7.5% TFE content with Black Pearls 2000 carbon. Two used .012" thick cathodes of 15% TFE content using Shawinigan carbon black. All cathodes utilized were of dimensions .95" wide by 1.375" tall. Separator utilized was .004" thick Manninglas 1200 double U-wrapped around the cathodes. This allowed a design of 26 cathodes and 27, .010" thick Ca anodes in the standard 1.2" wide D-cell. The third Black Pearls cathode cell was constructed with only 22 cathodes and 23 anodes with the intention of testing "tight" versus "loose" cell stack performance. The electrolyte used was 2:1, using Witco AlCl_3 , Fluka LiCl and Kodak SOCl_2 . The activation apparatus used allowed a vacuum to be pulled on the cells, then the line could be switched to the electrolyte reservoir, which was padded with 3-4 psig of Argon behind the electrolyte. The load used on the cells was 0.09 ohm, with the cells being activated under load.

An activation attempt was made on the first cell, a full-stack Black Pearls

TABLE 65 - HIGH SALT ELECTROLYTE MATRIX

ALL CELLS DISCHARGED WITH 25 OHM LOAD

TRIAL	CATHODE TYPE	CATHODE SIZE(INCHES)	ELECTRO- LYTE	DISCHARGE TIME(MIN)	OCV	\bar{V}	AHr	A-Hr/ CM ³
A	1 Shawinigan 7.5%TFE	.012x.685 x.540	2:2	10.5	2.84	2.2	.015	.22
	2 Pasted/ Baked			9.5	2.81	2.18	.014	.197
B	1 Black Pearls 7.5% TFE	.012x.685 x.540	2:2	15	2.77	2.33	.02	.286
	2 Pasted/ Baked			13	2.78	2.33	.02	.286
C	1 Black Pearls 15% TFE	.012x.685 x.540	2:2	8.25	2.79	2.22	.013	.171
	2 Pasted/ Baked			2.5	2.77	2.10	.003	.043
D	1 Ketjenblack 7.5% TFE	.012x.685 x.540	2:2	16.25	2.81	2.27	.024	.351
	2 Pasted/ Baked			15	2.82	2.30	.023	.328
E	1 Ketjenblack 15% TFE	.012x.685 x.540	2:2	16	2.8	2.28	.024	.347
	2 Pasted/ Baked			12	2.8	2.2	.018	.251
F	1 Shawinigan 7.5% TFE	.012x.685 x.540	3:3	5	2.81	2.1	.007	.100
	2 Pasted/ Baked			4.5	2.78	2.11	.006	.086
G	1 Shawinigan 7.5% TFE	.012x.685 x.540	4:4	1	2.92	2.14	.001	.014
	2 Pasted/ Baked							

Cathode cell. The cell only ran approximately 1.5 minutes above 2.0 volts, with heavy gassing visible passing back into the electrolyte reservoir. Subsequent examination showed that this cell had only partially activated due to an activation system vacuum leak.

After curing the vacuum leak in the activation system, a full-stack Shawinigan cathode cell was activated. This time, the cell received approximately 25 ml of 2:1 electrolyte before back-gassing to the reservoir became evident. The fill tube to the cell was heavily hand crimped when this occurred. This cell had also been activated under a 0.09 ohm load. The cell managed 2 minutes above 2.0 volts, reaching a maximum of 2.0 volts before the 150-psi cell vent activates to terminate the discharge.

These two cells were returned to the lab and the cell headers were cut off. The opened cells were manually activated with 25 ml of 2:1 electrolyte while under a 0.09 ohm load. Both rose above 2.0 volts and ran for approximately 2 minutes before electrolyte boiling away dropped the load voltage below 2.0. Under this load, the cells were producing 20 amps, a cathode loading rate of approximately 45 ma/cm².

The third cell activated, the second full-stack Black Pearls cathode cell, lost a discharge lead 45 seconds after activation began, halting discharge. At this point the cell had attained a voltage of only 1.47, giving a 15 amp delivery rate. The cell was continuously gassing after activation through failure to achieve a complete hand seal on the fill tube.

The fourth cell activated, the short-stack Black Pearls cell, also failed to reach 2.0 volts, reaching a maximum of 1.79 volts at 18 amps 1.25 minutes after activation. This cell also could not be completely hand sealed by crimping the fill tube and gassed continuously during discharge.

The fifth cell activated, the second 15% TFE Shawinigan carbon cathode cell, activated more fully, although it too began gassing immediately and could not be completely sealed by hand crimping. This cell vented via the vent sticker 3.5 minutes into the discharge. Data for voltage and amp rate during discharge are given below for cell No. 5:

<u>MINUTES AFTER ACTIVATION</u>	<u>LOAD VOLTAGE</u>	<u>AMPS</u>	<u>MINUTES AFTER ACTIVATION</u>	<u>LOAD VOLTAGE</u>	<u>AMPS</u>
0	1.99	20	2.0	2.15	22
.25	1.99	20	2.25	2.14	22
.75	2.04	20	2.5	2.13	22
1.0	2.06	21	2.75	2.08	21
1.25	2.09	21	3	1.99	20
1.5	2.11	21	3.5	1.24	13

The last three cells were autopsied. Cells three and four presented very similar aspects. The cells were dry, with the calcium tarnished and white coated. The separation was adhering to both anodes and cathodes. Some swelling of the cathodes had occurred. The fifth cell, which activated more fully and vented, presented a similar appearance except that the teflon wrapper around the cell stack was severely burnt and darkened.

Cell performance in this series was so poor that no meaningful choice of carbons could be made. Glass test cell data had given an edge to the Black Pearls 2000 carbon. However, the limited supply of Black Pearls 2000 carbon on hand necessitated the remaining cell work be done using the Shawinigan 50% compressed.

SECTION XIII

HIGH PRESSURE RESERVE CELL WORK

13.1 Improved Activation System

The original activation system had revealed several problems. One problem was that the low pressure delivery system filled the cells so slowly that back-gassing from the cells was interfering with complete activation. The other main problem was the difficulty of hermetically sealing the cell after activation. The variation in sealing allowed back-gassing from the cells, making comparison difficult.

Several changes were made in the activation assembly to eliminate these problems. The electrolyte reservoir could be clamped into an aluminum restraint fixture, allowing the delivery pressure on the PTFE reservoir to be raised to 21 psig. All fittings down to the cell fill tube were made a minimum of one-quarter inch id allowing higher flow. The cell sealing problem was solved by replacing the .060 inch id, fill tube with a .090 inch id tube terminating in a Swagelock ^(R) fitting, allowing the cell to be reliably attached to the activation assembly. Cell vacuum and electrolyte delivery was controlled by a teflon electrically-activated solenoid valve, allowing remote activation. A Swagelock ^(R) check valve was in place just below the electrolyte valve, so that the assembly would seal off the cell as soon as the internal cell pressure rose above the 20 psi of the delivery system. A 1000 psi pressure gauge to monitor cell pressure was also added to the assembly.

13.2 2:1 Versus 2:2 Electrolyte Cells

Two stainless steel rectangular D-cells were constructed. The cathodes were of pasted/baked construction utilizing 10% TFE and Shawinigan carbon. Twenty-six cathodes of dimensions 1 inch by 1½ inch by .010 inch were utilized. Since the Manning separator used in earlier series had required double-wrapping to cut down on shorts during construction, .012 inch thick Dexter 255 separator, U-wrapped around the cathodes, was used for these cells and proved to be easier to work with than had been the Manninglas^(R). Twenty-seven anodes of .010 inch thick polished calcium were used for the cells. Collector grid was rolled into the anodes with a hand rolling mill, as this had proven to be a reliable technique for preventing anode/grid separation.

The first cell was activated under a 0.09 ohm load using 2:1 AlCl₃/LiCl in thionyl chloride electrolyte.

The solenoid valve was rated at 30 psi (water back pressure). The pressure gauge on the system rose to 100 psi on activation and held steady there. Bubbling back along the electrolyte feed line indicated the check valve had not seated properly, allowing the solenoid valve to "see" the 100 psi system pressure and leak. A few seconds after 3 minutes into the discharge system, pressure instantly dropped to zero, then climbed steadily to 250 psi when at 3.6 minutes cell failure occurred, after which pressure slowly but steadily decayed to zero psi within one-half hour. Post activation inspection of the activation assembly revealed the cause of the sudden pressure drop. A coupling fitting seal had given way, venting system pressure, then had "salt-sealed". This was a lucky chance occurrence, as the jar to the system cleared the check valve, which then seated properly, sealing the system, as evidenced by lack of gassing through the solenoid valve.

Post-discharge cell post mortem showed that the sudden cell failure was due to the cell distortion at the 250 psi pressure snapping a cell stack lead. Otherwise, internally the cell components were intact, with electrolyte present, and badly tarnished calcium anodes present. Data taken during the discharge is given in Table 66 below:

TABLE 66 - RESERVE CELL DISCHARGE

<u>MINUTES ELAPSED TIME</u>	<u>VOLTS</u>	<u>AMPS</u>
0	2.042	20
15 (secs)	2.177	21
30 (secs)	2.017	20
45 (secs)	2.144	21
1	2.194	21
1.25	2.225	22 \bar{V} - 2.2
1.5	2.251	22 \bar{V} - 21
1.75	2.283	22 load - 0.09 ohm
2	2.328	23 V _{Hr} - 0.132
2.25	2.356	23 A _{Hr} - 0.006
2.5	2.366	23 Watt Hr - 0.014
2.75	2.326	23 A _{Hr} /cm ³ - 0.0005
3	2.219	22
3.25	2.12	21
3.5	1.988	20
3.6	0	0

The second cell was activated using the higher pressure, modified activation system. The only difference between the activation of this cell and the previous cell was that the electrolyte employed was 2:2 AlCl₃/LiCl in SOCl₂ to see if the acid-balanced electrolyte would stop the corrosive

attack and outgassing. Also, the vent sticker on this cell was manually deactivated to prevent normal venting. Table 67 gives the discharge data obtained with this cell.

TABLE 67 - 2:2 ACTIVATED RESERVE CELL

<u>VOLTS</u>	<u>AMPS</u>	<u>PRESSURE</u>	<u>ELAPSED TIME</u>	
			<u>MINUTES</u>	<u>SECONDS</u>
1.362	17	20	0	0
2.006	19	20	0	15
2.072	20	20	0	30
2.151	21	20	0	45
2.212	22	20	1	0
2.228	22	20	1	15
2.256	22	20	1	30
2.269	22	20	1	45
2.293	22	20	2	0
2.313	23	20	2	15
2.327	23	60	2	30
2.297	23	80	2	45
2.139	21	100	3	0
1.758	17	150	3	15
1.202	11	200	3	30
0.882	8	300	4	30
0.988	10	400	4	50
1.192	12	500	5	10
1.46	14	700	5	40
1.509	15	700+	5	50

The cell only remained above 2.0 volts for approximately 3 minutes after activation and when carrying an average of 22 amps, only about two-thirds of the desired load of 31 amps. The drastic pressure rise was experienced after cell voltage had fallen below 2.0, and was only halted by cell can distortion popping one of the soldered discharge leads loose from the can side.

Autopsy showed the cell stack to be intact despite a severely swelled casing. The cathodes had swelled, but only enough to fill the casing, so that the stack slid easily from the body. This had allowed the stack to rise in the casing as the cell header domed instead of snapping the internal lead. Free liquid electrolyte was present in the case and could be squeezed from the cell stack. The calcium anodes were intact, although tarnished.

Both cells, with balanced and unbalanced ($\text{AlCl}_3\text{:LiCl}$ ratios) electrolytes evidenced potentially disastrous pressure rises. The one advantage shown by the balanced (2:2 $\text{AlCl}_3\text{:LiCl}$) electrolyte was that the pressure rise occurred later in the discharge.

13.3 Cell Gassing Investigation

A simple apparatus was set up to allow gas from an ampoule to be passed through a gas bubbler frit. Since it was assumed that the gasses produced would be either mainly or entirely acidic (SO_2 and HCl), the gas washing assembly was filled with 50 ml of a 0.508N sodium hydroxide solution to act as an acid gas trap. 1.0g of either Ca or Li was allowed to react with electrolyte. 2:2 AlCl_3 to LiCl electrolyte was employed first. Within a 4 hour span the reaction rate at room temperature was negligible. 3:1 AlCl_3 to LiCl electrolyte was next employed to speed the reaction progress. 1.0g

Ca metal reacted to completion in 26 minutes, as judged by visual observation of the ampoule and cessation of gassing. 1.0g of Li reacted to the same stage in 20 minutes. Titration of the gas washing NaOH solution from the Ca ampoule revealed that the solution had gone entirely acidic, requiring 51.8 ml more of NaOH to return the solution to neutrality. The scrubber solution from the Li ampoule required a total of 4.6 ml of the .508 N NaOH to reach neutrality. On an equivalents basis, the Ca ampoule, containing 0.025 mole Ca, or 0.05 equivalent, produced .055 equivalent of gas. The Li ampoule, containing 0.14 equivalent of Li, produced 0.021 equivalent of gas. Weight for weight figured as SO_2 , the Ca produced 2.6 times as much gas. Equivalent for equivalent, the calcium ampoule produced 7.3 times as much gas.

Since glass test cells of single cathode/anode design had never evidenced symptoms of heavy gassing, two multi-cathode glass test cells were constructed using the same materials as for the full-sized reserve cells, except for Ketjenblack ^(R) carbon being used in the cathodes. These cells were of three cathode, four anode design. Dimensions of both anodes and cathodes were 1 inch by 1 inch. An external 2.0-ohm resistor, was used as a load.

Initial voltage under load was 2.5 for both cells, yielding a current density of 32 ma/cm^2 . Voltage decayed slowly in the glass cells to approximately 1.0v within 15 minutes. By 30 seconds into the discharge a vigorous reaction had ensued around the cell stack, giving the appearance of a full "rolling boil" taking place. That this reaction was taking place only at the cell stack was evidenced by the remainder of the flooded cell's electrolyte showing no bubbling. The very vigorous reaction continued unabated for approximately 5 minutes, then slowly abated over about the next 10 minutes.

By the time discharges were halted at 0.5v, the heavy glass test cells were noticeably warm through the heavy glove box gloves. Other single cathode/anode glass cells were constructed using the identical components to the three cathode/four anode cells. These were then discharged using a proportionately higher-valued resistor, without a sign of any gas-releasing reaction taking place.

13.4 Lower Rate Reserve Cells

The series of reserve cell discharges reported on in Section 13.2 was continued at increasing discharge resistances. Cell construction was identical with that used for the first two cells, except that a pleat-folded tab connector was used to attach the cathode leads to the terminal pin in the cover. This was to prevent breaking the lead in the event of gross can swelling. The first cell of this series, designated RES 11, was activated, under load, with the electrolyte system delivering 2:1 electrolyte at 20 psi. The check valve on the system did not seal fully for approximately 5 minutes after activation, holding the cell pressure to approximately 50 psi before the valve seated fully, allowing a fast pressure rise to begin. The discharge rate was between 11 and 12 amps. The cell stayed above 2.0 volts for 8.1 minutes. Discharge curves for pressure/voltage and temperature vs time for the cell are given as Figures D-1 and D-2, respectively, in Appendix D of this report. Temperature was measured by a thermocouple taped to the cell on a face perpendicular to the cell stack.

The second cell of the series, designated RES 12, was activated under load with 2:1 electrolyte, but without the activation system being pressurized.

Electrolyte delivered was determined by the vacuum on the system pulling electrolyte into the cell. With this cell, similarly to RES 11, the check valve failed to seal completely during the first 6 minutes of discharge, holding down initial stages of the pressure rise. After about 6 minutes into the discharge, the valve seated more fully, allowing the typical pressure rise, however, the valve never did seal completely, thus holding down the ultimate pressure the cell reached. This cell ran at a current draw rate of approximately 10 amps and stayed above 2.0v at this rate for 6.7 minutes. Since this cell ran for a shorter length of time, and still achieved 500 psi pressure with a leaking valve, it was decided that the additional head room created by a vacuum - only electrolyte delivery was not of value in holding down pressure rise and so the remainder of the cells in the series were activated using the pressurized electrolyte delivery system. Discharge curves for pressure/voltage and temperature vs time for the cell are given as Figures D-3 and D-4 respectively, in Appendix D to this report. Temperature was measured by a thermocouple taped to the cell can on a face perpendicular to the cell stack.

The third cell of the series, designated RES 6, was activated under load with 2:1 electrolyte, and discharged at a load rate of between 9 and 10 amps. The cell remained above 2.0v at this draw rate for 6.8 minutes, by which point the pressure had risen to almost 600 psi, causing a failure inside the cell, dropping the cell voltage instantly to zero. At this point the temperature measured on the cell casing on a side parallel to the cell stack was 110°C. Approximately 3 minutes after the cell had experienced internal failure, temperature and pressure, which had been slowly falling, began rising, the

pressure quite steeply. Within 30 seconds the pressure had risen from 400 psi to 1200 + psi, pegging out a 1000 psi gauge on the system. At this point the casing ruptured quite violently. The cell casing was propelled downward with sufficient force to shatter the steel ring stand the activation assembly and cell were supported by. The cell header was sheared from the activation assembly, and was not recovered. Cell stack components were scattered in a 15 foot circle around the test pad. Many of the anodes recovered still showed almost complete Ca coverage, with only the edges being bare, and were still wet with electrolyte. Discharge curves for pressure/voltage and temperature vs time for the cell are given as Figures D-5 and D-6 respectively, in Appendix D of this report.

The fourth cell of the series, designated RES 7, was activated, under load, with 2:1 electrolyte and discharged at a rate of between 10 and 11 amps. The cell remained above 2.0v for 7.6 minutes. At this point cell voltage was still 2.7v when an external lead came free from can warpage. Internal cell pressure at this point was 780 psi. Cell temperature, measured on the can on a side perpendicular to the cell stack, was 207°C at this point. Following the load removal on the cell, both temperature and pressure declined slowly until the cell could be manually vented. Discharge curves for pressure/voltage and temperature vs time for the cell are given as Figures D-7 and D-8, respectively, in Appendix D of this report.

The fifth cell of the series, designated RES 8, was activated under load, with 2:1 electrolyte, and discharged at an 11 amp rate. At 6 minutes into the discharge, when the cell was at 2.695 volts, internal pressure caused an internal cell failure, dropping voltage to zero and halting the discharge.

Temperature at this point, measured on the can surface on a face parallel to the cell stack, was 167°C and internal cell pressure was 600 psi. Following the cell failure both temperature and pressure slowly declined to where the cell could be manually vented. Discharge curves for pressure/voltage and temperature vs time for the cell are given as Figures D-9 and D-10 respectively, in Appendix D to this report.

The sixth cell of the series, designated RES 1, was activated under load, with 2:1 electrolyte, and discharged at a rate of 10 amps. The check valve on the system failed to seal completely and instead of allowing the pressure to rise indefinitely, functioned as a blow-off valve, holding the pressure at 50 ± 10 psi. Cell discharge life with the pressure being bled off was not any better than the cells where the pressure rose unchecked, running 7.6 minutes above 2.0 volts. However, the skin temperature of this cell was noticeably lower, rising to a little over 80°C , measured at a can face perpendicular to the cell stack, then holding quite stable around 80°C . Discharge curves for pressure/voltage and temperature vs time for the cell are given as Figures D-11 and D-12 respectively, in Appendix D of this report.

The seventh cell of the series, designated RES 2, was a virtually identical discharge to that of RES 1. The cell was activated under load, with 2:1 electrolyte, and discharged at a rate between 10 and 11 amps. The check valve allowed outgassing, holding the pressure at 50 psi after an initial rise to 70 psi. Temperature of the cell skin, at a face perpendicular to the cell stack, did a slow rise, staying in the 60°C range during discharge.. The cell achieved 7.6 minutes above 2.0 volts under the load. Discharge curves for pressure/voltage and temperature vs time for the cell are given as Figures D-12 and D-14 respectively, in Appendix D of this report.

The eighth cell of the series, designated RES 3, was a similar discharge to RES 1 and RES 2. The cell was activated under load with 2:1 electrolyte, and discharged at an 11 amp rate. The check valve allowed outgassing, holding the pressure virtually constant at 30 psi. As with the other cells, the course of the discharge remained unaffected. The cell achieved 7.8 minutes above 2.0v under the load. However, apparently in correlation with the lower pressure, the cell skin temperature, at a face perpendicular to the cell stack, was the lowest of any cell discharged, reaching a maximum of only 62°C and actually decreasing slightly after reaching this maximum. Discharge curves for pressure/voltage and temperature vs time for this cell are given as Figures D-15 and D-16 respectively, in Appendix D of this report.

The ninth cell of the series, designated RES 4, was activated under load, with 2:1 electrolyte, and discharged at a rate of 11 amps. The check valve sealed properly, allowing pressure to rise without hindrance. At 6.7 minutes into the discharge, an internal cell failure halted the discharge, dropping cell voltage to zero. Cell pressure at this point was 800 psi. Temperature data for this cell could not be taken, as the thermocouple failed as the cell was activated. A discharge curve for the pressure/voltage vs time for the cell is included as Figure D-17 in Appendix D of this report.

The tenth cell of the series, designated RES 5, was activated under load, with 2:1 electrolyte and discharged at a rate of 11 amps. The check valve sealed properly, allowing continuous pressure rise. The cell achieved 8.8 minutes above 2.0 volts at which point the pressure was above 1000 psi and temperature of the cell skin was 158°C, measured at a cell face perpendicular to the cell stack. At 9 minutes into the discharge a cell seam gave, allowing a fairly rapid venting of the cell. At 15 minutes into the discharge with the cell voltage at 1.6 and pressure at 350 psi, calcium ignited inside the cell, burning through a lower edge of the can. The can spit sparks and

emitted copious quantities of white smoke before gradually ceasing to burn. Discharge curves for pressure/voltage and temperature vs time for the cell are given as Figures D-16 and D-17 respectively, in Appendix D of this report.

The eleventh cell of the series, designated RES 9, was activated under load, with 2:1 electrolyte, and discharged at a rate of 7 amps. The cell achieved 13.8 minutes above 2.0 volts under the load. At 9.8 minutes into the discharge, with pressure at 980 psi, something in the discharge set up gave way slightly, slowly dropping the pressure to about 900 psi, after which it began a slow climb to 1000 psi.. Leakage then began again, slowly lowering pressure during the remainder of the discharge. The temperature curve closely reflects the course of the pressure curve. Discharge curves for pressure/voltage and temperature vs time for the cell are given as Figures D-20 and D-21 respectively, in Appendix D of this report.

The last cell of the reserve series, designated RES 10, was activated under load, with 2:1 electrolyte, and discharged at a rate of 7 amps. The cell achieved 13.8 minutes above 2.0 volts under the load. Pressure had peaked at 950 psi about 9.8 minutes into the discharge, when a cell seam began leaking, steadily venting the pressure. Temperature, which had reached 145°C, as measured on the cell skin at a face perpendicular to the cell stack, also began a slow fall at this time. Discharge curves for pressure/voltage and temperature vs time for this cell are given as Figures D-22 and D-23 respectively, in Appendix D of this report.

SECTION 14

CONCLUSIONS/RECOMMENDATIONS

14.1 Active Cell Conclusions

Two major unresolved problem areas emerged from the work accomplished on the calcium-thionyl chloride system. By far the most serious problem was the inability to develop an electrolyte salt, both stable relative to calcium and still capable of supporting a 400 ma draw rate with reasonable discharge life. Both LiAlCl_4 and $\text{Ca}(\text{AlCl}_4)_2$ based electrolytes were corrosive towards the calcium anode within at most a few weeks' time. Moisture level in the electrolyte, at least down to approximately 100 mg/l, did not materially affect corrosion rate or onset.

Dissolution of LiAlCl_4 in benzoyl chloride, followed by dilution with thionyl chloride at varying percentages, did produce an electrolyte stable towards calcium, at least for the duration time of the storability study (5 months' time). The gain in storability of the cell system by use of benzoyl chloride must be balanced against a steep loss in discharge life and current draw capability.

A wide variety of alternative electrolyte salts/inhibitors/additives were investigated. Of those that showed preliminary compatibility/storability with calcium, none investigated showed sufficient solubility to produce an electrolyte, or where they were sufficiently soluble, failed to produce open circuit voltages above 2.0 volts.

The second area unresolved in the development of the desired cell is a cathode sufficiently tolerant of discharge product plugging. Cathode discharge life for the desired 14 AH cell requires the cathode utilization rate to approach 1.2 AH/cm^3 . As developed, cathodes for the active cell produced $0.5\text{--}0.7 \text{ AH/cm}^3$, leaving the as-designed cells decidedly cathode limited.

14.2 Active Cell Recommendations

Central to the development of a viable calcium-thionyl chloride cell is development of an electrolyte capable of supporting a reasonable current draw rate and stable with respect to calcium. Further work with aluminum containing electrolyte salts appears futile, unless a co-solvent besides benzoyl chloride can be found, capable of stabilizing LiAlCl_4 or $\text{Ca}(\text{AlCl}_4)_2$ relative to calcium, and itself capable of supporting cell discharge.

Although distinctly secondary to the necessity of a calcium-stable electrolyte, an improved cathode is a necessity for a cell of the desired high energy density. A porous cathode, perhaps made by the dissolved wax method, which would allow expansion to be taken up internally and provide enhanced surface area, would be a logical area for investigation.

14.3 Reserve Cell Conclusions

From the discharge results obtained, it does not appear possible to produce a cell using $\text{AlCl}_3/\text{LiCl}$ electrolyte that will sustain a 31 amp discharge above 2.0 volts. At a 22 amp discharge rate, cells stayed above 2.0 volts for only 3 minutes or less. As well, the heat produced by the high rate discharges increases the corrosive attack by the electrolyte on the calcium anode to the point that cell pressures in excess of 700 psi have been observed in as little as 5 minutes. The extremely quick pressure rise observed at rates as low as 7 amps make it unlikely that a practical reserve cell can be produced, at least with acidic electrolyte.

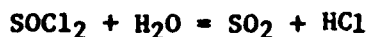
14.4 Reserve Cell Recommendations

The severe gassing associated with aluminum containing electrolyte salt indicate that any further development work should concentrate on finding an alternate salt. Although the work accomplished was scarcely conclusive, cobalt phthalocyanine as a cathode additive showed promise to hold down cell temperatures during discharge.

SECTION 15
SAFETY ANALYSIS

15.1 Active Cell Safety Considerations

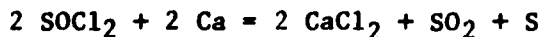
The thionyl chloride used as a cathode in the calcium-thionyl chloride cell presents a hazard in the utilization of these cells. Breaching of the cell would release thionyl chloride, which is highly toxic and corrosive. Contact with thionyl chloride liquid can damage mucous membranes, eyes and skin. Although thionyl chloride is a liquid at room temperature (+20°C), vapor pressure is high (87 mm. Hg), with a boiling point of only 79°C. In moist air, thionyl chloride reacts in line with the following equation:



Both byproducts of water reaction, SO₂ and HCl, are themselves acidic and extremely irritating to mucous membranes. SO₂ is gaseous and HCl is extremely volatile. A spill or release of liquid thionyl chloride will produce immediate and serious airborne contamination.

Liquid thionyl chloride may be neutralized with sodium bicarbonate (NaHCO₃) or lime (CaO or Ca(OH)₂), followed by flushing down with a water spray. However, since volatile SO₂ and HCl will be formed during neutralization of the thionyl chloride, care must be taken to ensure that the water spray holds down the vapors, allowing the lime or soda to react with the acids formed.

Under typical discharge conditions, the overall reaction between thionyl chloride and calcium is represented by the following equation:



As the SO_2 produced during discharge is soluble in thionyl chloride, at low discharge rates where the production of SO_2 is also low, pressure in the cell should not increase significantly. However, as shown by the Proof-of-Concept cells placed in hot ($+ 74^\circ\text{C}$) storage (see Section 9.6 of this report), an electrolyte not completely stable towards the calcium anode can initiate a sufficiently vigorous corrosion reaction to vent the cell, creating a personnel hazard.

15.2 Reserve Cell Safety Considerations

From the discharge tests run with cells in a reserve configuration, it is apparent that cells using AlCl_3 -based electrolytes will inevitably produce sufficient gas to vent the cell. Once cell temperature reaches the vicinity of 60°C the reaction accelerates. Pressure can rise at a rate exceeding 100 psi per minute while under load.

One cell that shorted while under discharge produced internal temperatures sufficient to ignite the calcium metal anodes. The ensuing reaction was vigorous enough to burn through the stainless steel cell casing.

Considering the foregoing observations, a calcium reserve cell, in addition to the hazard associated with the thionyl chloride-based electrolyte, poses a distinct danger of venting or explosion. A cell equipped with a pressure relief valve could ameliorate the discharge hazards to a significant extent. However, the solid crust of salt left behind by vaporizing electrolyte is capable of sealing apertures and retaining quite high pressures. Reliability of a vented design would in consequence need to be quite high.

APPENDIX A

PINNACLE RESEARCH INSTITUTE REPORT

ELECTROCHEMICAL STUDIES OF CALCIUM IN THIONYL CHLORIDE

Final Report

12/30/82

Pinnacle Research Institute, Inc.

10432 N. Tantau Avenue

Cupertino, California

Abstract

Kinetics and mechanism of the anodic dissolution of Ca in $\text{LiAlCl}_4/\text{SOCl}_2$ and $\text{Ca}(\text{AlCl}_4)_2/\text{SOCl}_2$ electrolytes were studied using rapid scan chronopotentiometric and galvanostatic polarization techniques. Preliminary results reveal that while the one-charge-transfer reaction via rapid scan chronopotentiometric polarization involves the adsorption of AlCl_4^- on the metal surface for both electrolytes, the steady-state two-charge-transfer reaction via galvanostatic polarization shows distinctly different mechanisms for each electrolyte. In LiAlCl_4 electrolyte, a pure charge transfer reaction is observed and the reaction rate is independent of the electrolyte concentration. In $\text{Ca}(\text{AlCl}_4)_2$ electrolyte, however, the charge transfer reaction is accompanied by AlCl_4^- adsorption and the rate of anodic dissolution depends on the electrolyte concentration.

Introduction

This program was undertaken to develop a fundamental understanding of the inner working of the calcium electrode in the Ca - SOCl_2 system under the Purchase Order No. FC 85269 from the Eagle - Picher Industries, Inc.

The problems of voltage delay and safety associated with Li - SOCl_2 cell has prompted the search for other alternative metal - SOCl_2 high energy density battery systems. . . Calcium which possesses volumetric capacity equivalent to lithium but with much higher melting point (838°C compared to 179°C for Li) has been identified by U.S. Air Force as the leading candidate to supplement the shortcomings of lithium. However, the development of Ca - SOCl_2 system has been hampered by high corrosion rate of calcium. In order to mitigate this corrosion effect, a basic understanding toward the corrosion processes of Ca in SOCl_2 electrolyte is inevitable. It is, therefore, the purpose of this investigation to establish the basic knowledge of the kinetics and mechanism of the anodic dissolution of calcium in the electrolytes of interest. The ultimate goal of this program is to eliminate the corrosion problem which has plagued the development of the Ca - SOCl_2 battery system.

Experimental

An inert atmosphere glove box system was set up for the handling of calcium metal and thionyl chloride solvent. The glove box is a Vacuum Atmospheres (VAC) Dri-Lab with the capability of maintaining an inert atmosphere with less than 10 ppm O_2 ; H_2O , and N_2 . Experimentation and sample preparation were normally carried out in atmospheres containing less than 100 ppm O_2 and H_2O . No attempt was made to remove N_2 due to its low reactivity with Ca. The atmosphere in the box was periodically purged with dry argon and solvent vapors were removed by means of a liquid nitrogen cold trap. An auxiliary glove box was also set up for experimentation and sample preparation which does not require the stringent atmospheric control provided by the VAC system.

The electrochemical cell utilized in these studies was constructed of Pyrex glass and is comprised of two compartments. The main reaction chamber is cylindrical with an inner diameter of 3.8 cm. It is fitted with a top, via a ground glass fitting, which has an electrical feedthrough to a cylindrical shaped Pt gauze counter (auxiliary) electrode. The counter electrode is centered in the main reaction chamber with an opening along the length of one side. An opening in the top is sealed to a 6 mm i.d. glass tube through which the working electrode, described below, is inserted. A straight tubing coupler is used to seal the

working electrode to the glass tubing.

The second chamber of the cell comprises the reference electrode compartment. It is formed by attachment of a side-arm tube to the main chamber with a capillary tip extending into the main chamber to a point very near the center. A AgCl coated Ag wire was used as the reference electrode.

The Ca metal working electrodes for insertion in the electrochemical cell were prepared from 1 inch diameter Ca metal rods obtained from Electronics Space Products, Inc. (854-56 S. Robertson Blvd., Los Angeles, California 90035). The purity was specified as 99.9% metals basis. the rods were reduced to 0.200 inch diameter on a lathe using a recirculating oil cooling system and very slow machining. There was no apparent work hardening during this process. The resulting rods, approximately 2 inches in length, were press fitted into an 0.250 inch o.d. Kel-F sheath and tapped on one end to accept a 4-40 thread. An 0.250 inch diameter brass rod, approximately 4 inches in length, was reduced to 0.200 inch diameter and tapped on one end to accept a 4-40 thread for electrical connection. The other end was fashioned with a 4-40 stud for attachment to the previously described Ca electrode. The brass rod was press fitted into a Kel-F sheath which was 0.250 inches o.d. on the lower 3 inches of its length and 5/16 inch o.d. on the remainder. This form allowed insertion into the cell and positioning

via the tubing coupler at the top of the cell. The brass section of this two-part electrode is thus reusable, while the Ca surface may be renewed by either machining, polishing, or replacement. The exposed Ca surface area was 0.21 cm².

High-purity SOCl₂ (Eastman Kodak), AlCl₃ (J.T. Baker, anhydrous, powder), and CaCl₂ (J.T. Baker, anhydrous, granular, 4 mesh) were dried where necessary and used without further purification. A supply of 1.8 M LiAlCl₄ was provided by Eagle-Picher and was used as received. The Ca electrodes were subjected to a surface preparation procedure to provide a reproducible surface prior to immersion in an electrolyte. Electrodes were treated prior to each electrochemical measurement, except those performed on electrodes subjected to storage tests. The surface preparation procedure consists of rough polishing with 400 grit polishing paper followed by final polishing with 600 grit paper. In both steps the paper is wetted with SOCl₂ during polishing. Polishing is performed in the glove box.

A glass reaction vessel was designed and fabricated to facilitate the preparation of electrolyte solutions consisting of SOCl₂, electrolyte salts, and AlCl₃. The vessel consists of a round bottom flask with three ground glass joints. Two of these joints accommodate small side-arm vessels which contain the AlCl₃ reactant. By rotation of the side-arm vessels, small additions of AlCl₃ can be made,

thus providing excellent control over the dissolution reaction. This technique, combined with immersion in an ice-water bath, allows the electrolyte to be prepared without over-heating.

All electrochemical experiments were performed using a Princeton Applied Research (PAR) Model 175 Universal Programmer and PAR Model 173 Potentiostat/Galvanostat for controlling the stimulus applied to the system under study. Responses were recorded on a Hewlett-Packard Model 7047A X-Y/T recorder. All experiments utilized a reference electrode to provide measurements of working electrode potential with as little contribution from uncompensated resistance effects as possible.

Several different electrochemical techniques were utilized during the course of this investigation. Each subjects the system under study to different stimuli, with responses controlled by various physical and electrochemical phenomena. A brief description of each of these techniques follows with a statement regarding their utility in the current application.

Potentiostatic Polarization - a technique in which the potential of the working electrode (Ca) is held constant while the current required to maintain that potential is monitored. In the case of metal dissolution, potentials anodic of the open circuit voltage are applied and the

resulting anodic current is monitored. The current observed is determined in part by the rate of dissolution of the metal at the set potential and by the rate of diffusion of reactants to and from the metal surface. In this technique only those electrochemical processes which occur at potentials equal to or more cathodic than the set potential can occur. In the present application, this technique provides information regarding the ability of the metal in a particular electrolyte to provide current with fixed or limited polarization.

Galvanostatic Polarization - this technique is complementary to potentiostatic polarization. In this case, the current through the working electrode is maintained constant while its potential is monitored. The controlling processes are the same as before, except that the potential is free to shift to any process required to maintain the preset current. Thus, the observed potential may represent a mixed potential from several different processes. This technique provides information regarding the ability of the electrode in a particular electrolyte to maintain a constant current drain, wherein the cell potential may be of secondary importance.

Rapid Scan Chronopotentiometry - in this technique the current applied to the electrode is increased rapidly and

the potential response of the electrode/electrolyte system is monitored. The rapidly changing current allows only those processes which can occur quickly to contribute to the observed potential. Thus, in the ideal case, the response should be identical to that observed for galvanostatic polarization. If, however, processes of varying speeds are occurring simultaneously, differences in the responses to the two techniques will be observed. Therefore, this technique provides information regarding the mechanism responsible for controlling the polarization and current delivering capability of a given system.

Results and Discussion

Figure 1 shows the variation of conductivity with respect to the concentration of LiAlCl_4 and $\text{Ca}(\text{AlCl}_4)_2$ in SOCl_2 . Four LiAlCl_4 and four $\text{Ca}(\text{AlCl}_4)_2$ electrolytes were prepared for galvanostatic and chronopotentiometric polarization studies.

a). Mechanism of Anodic Dissolution by Rapid Scan Chronopotentiometric Polarization

If the anodic dissolution of Ca is a single step reaction represented by $\text{Ca} \rightarrow \text{Ca}^{++} + 2\text{e}^-$, no effect of $[\text{AlCl}_4^-]$ on the anodic polarization curve should be observed. This, however, does not agree with the results from this study. Figure 2 shows the chronopotentiometric polarization of Ca in LiAlCl_4 electrolytes. Within the experimental error (i.e., $\pm 11\%$), the charge transfer reaction of Ca exhibits the same characteristics in various electrolytes, with Tafel slopes of ~ 126 mV/decade. However, the rate of anodic dissolution of Ca in each electrolyte is different.

To explain these results, a reaction involving AlCl_4^- ion is assumed for the anodic dissolution of Ca, that is



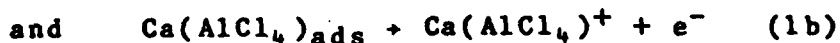
where $\text{Ca}(\text{AlCl}_4)^+$ is a complex ion at the metal surface.

Based on electrokinetics, the rate of this reaction can be derived if the rate determining step is established. Thus, if Equation (1) is a single step reaction, the rate would be given by

$$i = k[\text{AlCl}_4^-] \exp\left(\frac{2\alpha F}{RT} \cdot \eta\right) \quad (2)$$

where k is a constant, $[\text{AlCl}_4^-]$ is the concentration of AlCl_4^- , η is the overvoltage and the other symbols have their usual meanings.

From the standpoint of kinetics, Equation (1) may be further divided into two consecutive elementary steps



where $\text{Ca}(\text{AlCl}_4)_{\text{ads}}$ is an activated complex adsorbed on the metal surface.

For step (1a), the rate of overall reaction is given by

$$i = k_a[\text{AlCl}_4^-] \exp\left(\frac{\alpha F}{RT} \cdot \eta\right) \quad (3)$$

where k_a is a constant.

If step (1b) is rate determining, the derivation of the rate equation for the overall reaction will lead to two different results depending upon whether θ , the surface

coverage of $\text{Ca}(\text{AlCl}_4)_{\text{ads}}$, is $\theta \rightarrow 0$ or $\theta \rightarrow 1$. In both cases, the Langmuir adsorption isotherm can be applied.

The rate of step (1b) is then

$$i = k_b [\text{Ca}(\text{AlCl}_4)_{\text{ads}}] \exp\left(-\frac{\alpha F}{RT} \cdot n\right) \quad (4)$$

where k_b is a constant and $[\text{Ca}(\text{AlCl}_4)_{\text{ads}}]$ is the concentration of adsorbed $\text{Ca}(\text{AlCl}_4)$ on the surface.

Assuming that $\theta = K[\text{Ca}(\text{AlCl}_4)_{\text{ads}}]$, then

$$i = k_b' \theta \exp\left(-\frac{\alpha F}{RT} \cdot n\right) \quad (5)$$

where $k_b' = K \cdot k_b$.

Under conditions such that (1b) is the rate determining step, (1a) can be regarded as being in a quasi-equilibrium state when $\theta \rightarrow 0$. We may then, from the Langmuir isotherm, write

$$[\text{Ca}(\text{AlCl}_4)_{\text{ads}}] = k_a [\text{AlCl}_4^-] \exp\left(\frac{F}{RT} \cdot n\right) \quad (6)$$

where k_a is a constant. Substitution of Equation (6) into Equation (4) gives the rate of overall reaction

$$i = k_a k_b [\text{AlCl}_4^-] \exp\left[\frac{(1+\alpha)F}{RT} \cdot n\right] \quad (7)$$

When $\theta \rightarrow 1$, Equation (7) is no longer valid, and the rate is simply given by Equation (5), i.e.,

$$i = k_b' \exp\left(\frac{\alpha F}{RT} \cdot \eta\right) \quad (8)$$

Based on the rate expression given by Equations (2, 3, 7, and 8), the Tafel constant (η_a), and the $[\text{AlCl}_4^-]$ dependence of the reaction rate can be calculated for each reaction mechanism. Table 1 gives the results of these calculations.

By comparison of calculated results as shown in Table 1, one can verify the reaction mechanism. Figure 2 exhibits the polarization results by means of rapid scan chronopotentiometric techniques. As we can see from this figure, each line corresponds to one concentration of AlCl_4^- . Within the experimental error of $\pm 11\%$, all lines are fairly parallel. The average Tafel slope of these lines is 126 mV/decade. This Tafel slope value corresponds to a one charge transfer reaction with $\alpha = 0.5$. In this case, reaction (1a) as shown in Table 1 is strongly favored for the anodic dissolution of calcium in $\text{LiAlCl}_4/\text{SOCl}_2$ electrolytes when rapid scan chronopotentiometric polarization is employed.

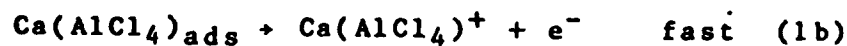
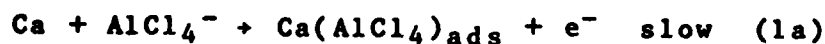
Table 1. Tafel Constant and $[\text{AlCl}_4^-]$ Dependence
of Anodic Dissolution of Calcium

Reaction Step	Tafel Constant* $\tau = n\alpha = \frac{RT}{F} \left(\frac{\partial \log i}{\partial \eta} \right)$	$[\text{AlCl}_4^-]$ dependence $\lambda = \left(\frac{\partial \log i}{-\partial \log [\text{AlCl}_4^-]} \right)$
$\text{Ca} \rightarrow \text{Ca}^{++} + 2\text{e}^-$	1	0
$\text{Ca} + \text{AlCl}_4^- \rightarrow \text{Ca}(\text{AlCl}_4)^+ + 2\text{e}^- \quad (2)$	1	1
$\text{Ca} + \text{AlCl}_4^- \rightarrow \text{Ca}(\text{AlCl}_4)_{\text{ads}} + \text{e}^- \quad (1a)$	0.5	1
$\text{Ca}(\text{AlCl}_4)_{\text{ads}} \rightarrow \text{Ca}(\text{AlCl}_4)^+ + \text{e}^- \quad (1b)$		
$\theta \rightarrow 0$	1.5	1
$\theta \rightarrow 1$	0.5	0

* assuming $\alpha = 0.5$

b). Mechanism of Anodic Dissolution by
Galvanostatic Polarization

Galvanostatic polarization curves were obtained for Ca in both $\text{LiAlCl}_4/\text{SOCl}_2$ and $\text{Ca}(\text{AlCl}_4)_2/\text{SOCl}_2$ electrolytes. Figure 3 shows the polarization of Ca in LiAlCl_4 electrolytes. Although the Tafel slope values are scattered, ranging from 33 to 50 mV/decade, the polarization curves exhibit no dependency on the concentration of AlCl_4^- . By comparing Figures 2 and 3 and from Table 1, it can be seen that the rate-determining step of the anodic reaction is shifting from Equation (1a) to a pure charge transfer reaction, i.e., $\text{Ca} \rightarrow \text{Ca}^{++} + 2\text{e}^-$, when the polarization format changes from rapid scan to steady-state. From previous results obtained for rapid scan polarization, it could be shown that the most probable mechanism for the steady-state anodic polarization of calcium in $\text{LiAlCl}_4/\text{SOCl}_2$ electrolytes is



The results of galvanostatic polarization of Ca in $\text{Ca}(\text{AlCl}_4)_2/\text{SOCl}_2$ electrolytes is summarized in Figure 4. A careful examination of Figures 3 and 4 reveals that there

are three distinct differences between the polarization characteristics of Ca in LiAlCl_4 and $\text{Ca}(\text{AlCl}_4)_2$ electrolytes. First, the Tafel slope of Ca in the calcium salt electrolyte is almost double that in the Li salt electrolyte, indicating that a faster rate is obtainable with the latter (aside from the fact that the conductivity of the Li salt electrolyte is higher than that of the Ca salt electrolyte). Secondly, there is a strong indication that the steady-state anodic dissolution of Ca in the Ca salt electrolyte depends on the concentration of AlCl_4^- and thus the reaction mechanism is controlled by Equation (2) rather than being a pure charge transfer reaction. The last distinct difference is the current density, i_c , at open circuit ($\eta = 0$). It is observed, from comparison of Figures 3 and 4, that i_c , which might be referred to as the corrosion current density if $i_c > i_0$ (the exchange current density), for the calcium salt electrolyte is at least one order of magnitude higher than that for the Li salt electrolyte. This difference might stem from the fact that the mechanisms of anodic dissolution in these two electrolytes are quite different. More elaborate experimentation is required to further elucidate the marked difference in kinetics and mechanism for the dissolution of Ca metal in LiAlCl_4 and $\text{Ca}(\text{AlCl}_4)_2$ electrolytes.

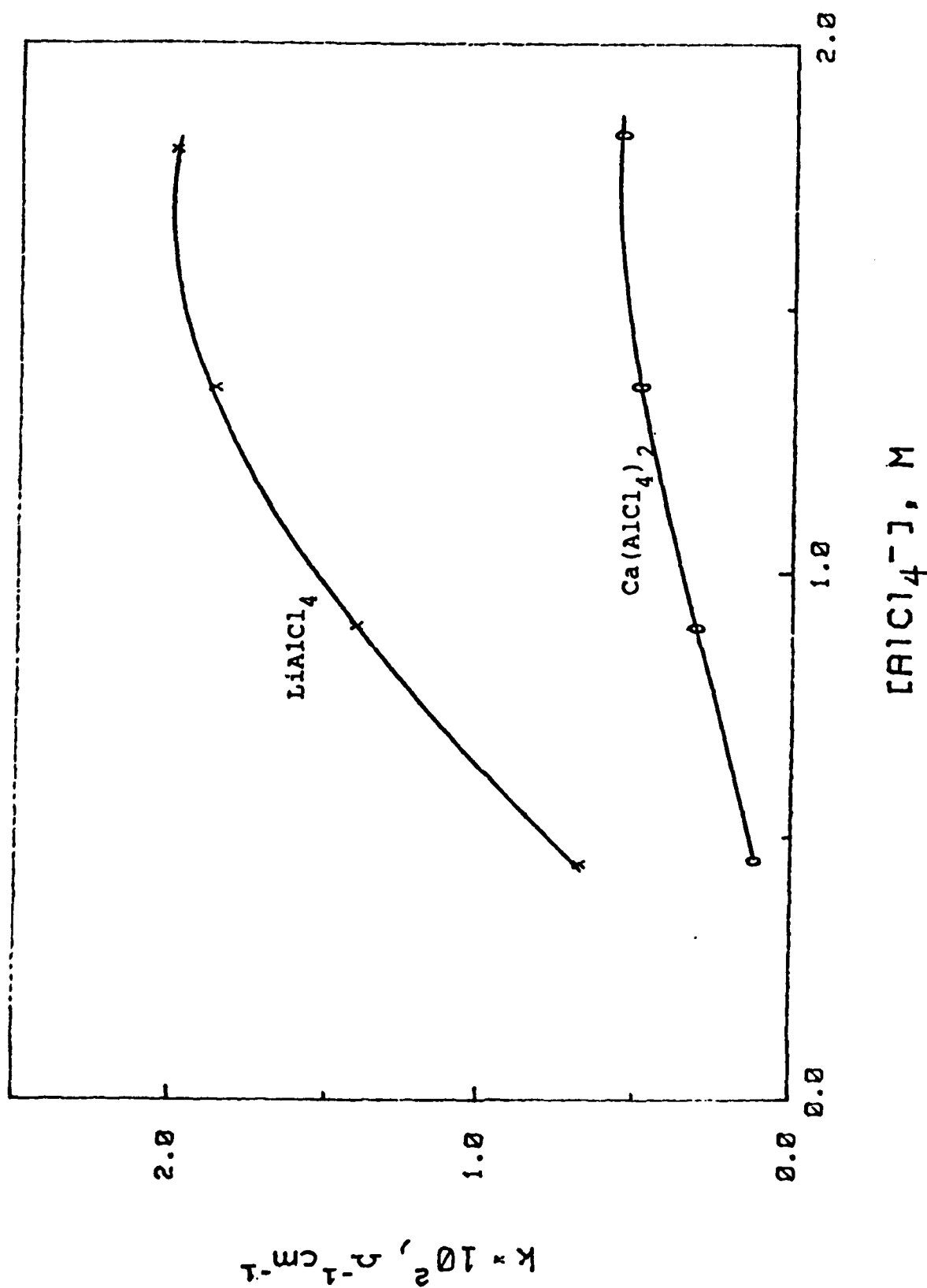


Figure 1. Variation of conductivity, k ($\Omega^{-1} \text{cm}^{-1}$), with respect to the concentration of LiAlCl_4 and $\text{Ca}(\text{AlCl}_4)_2$ in SOCl_2 .

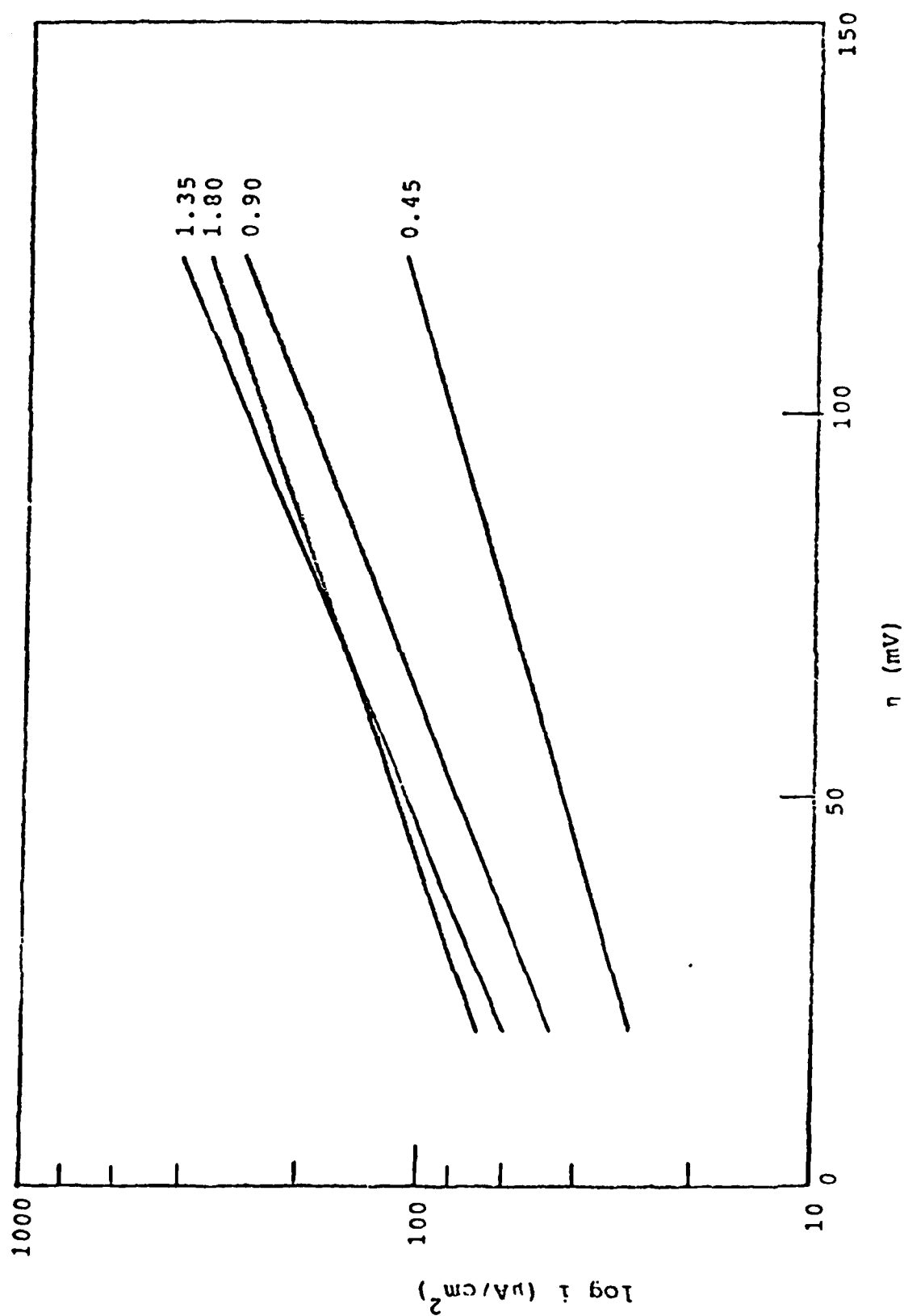


FIGURE 2 Rapid Scan Chronopotentiometric Polarization of Calcium in $\text{LiAlCl}_4/\text{SOCl}_2$ Electrolytes at Room Temperature. Sweep Rate: 1 mA/Sec.

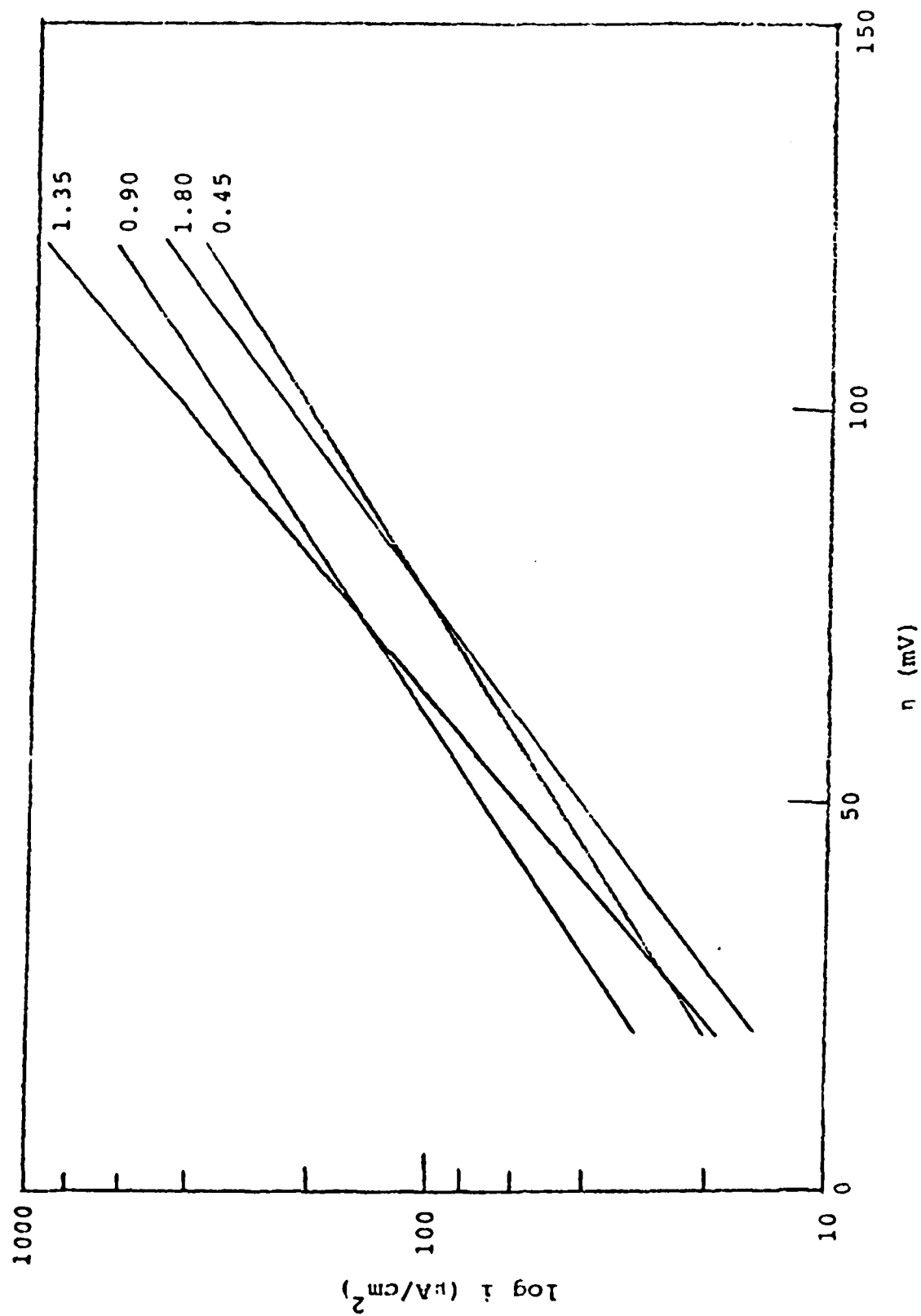


FIGURE 3 Galvanostatic Polarization of Calcium in $\text{LiAlCl}_4/\text{SOCl}_2$ Electrolytes at Room Temperature

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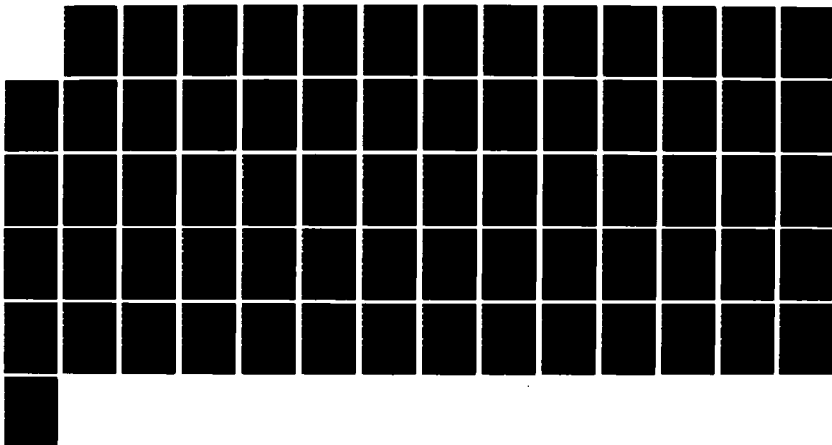
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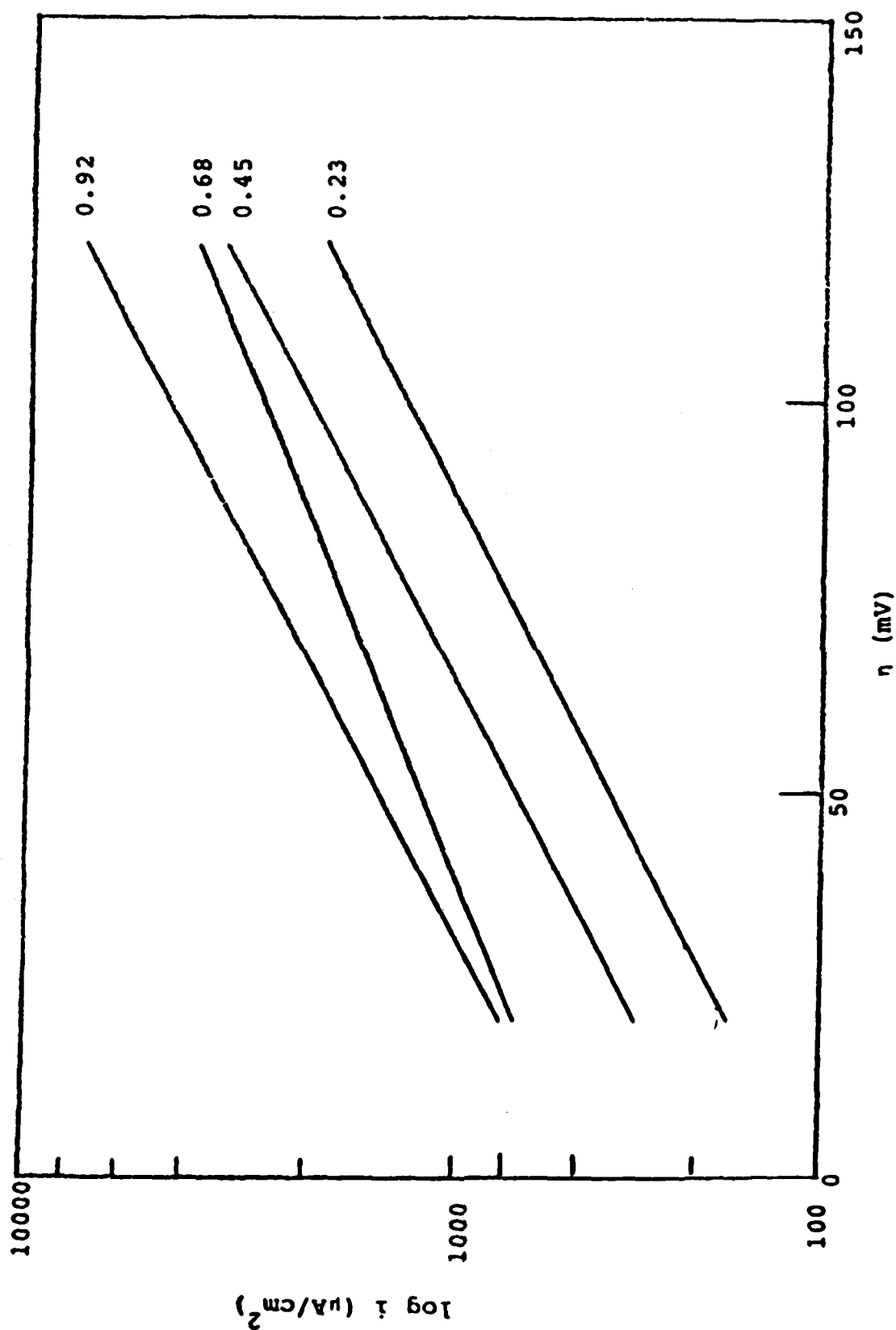
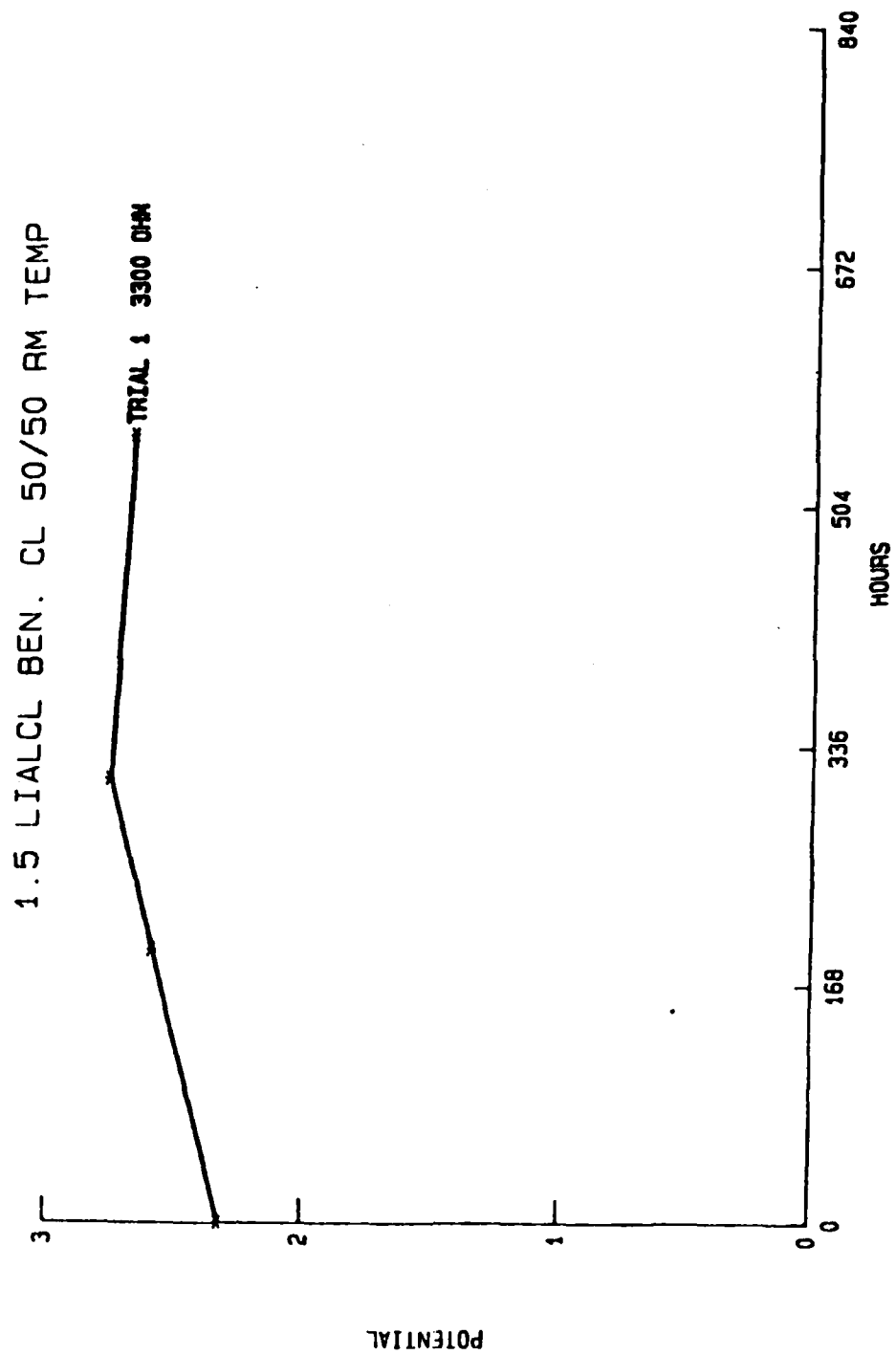
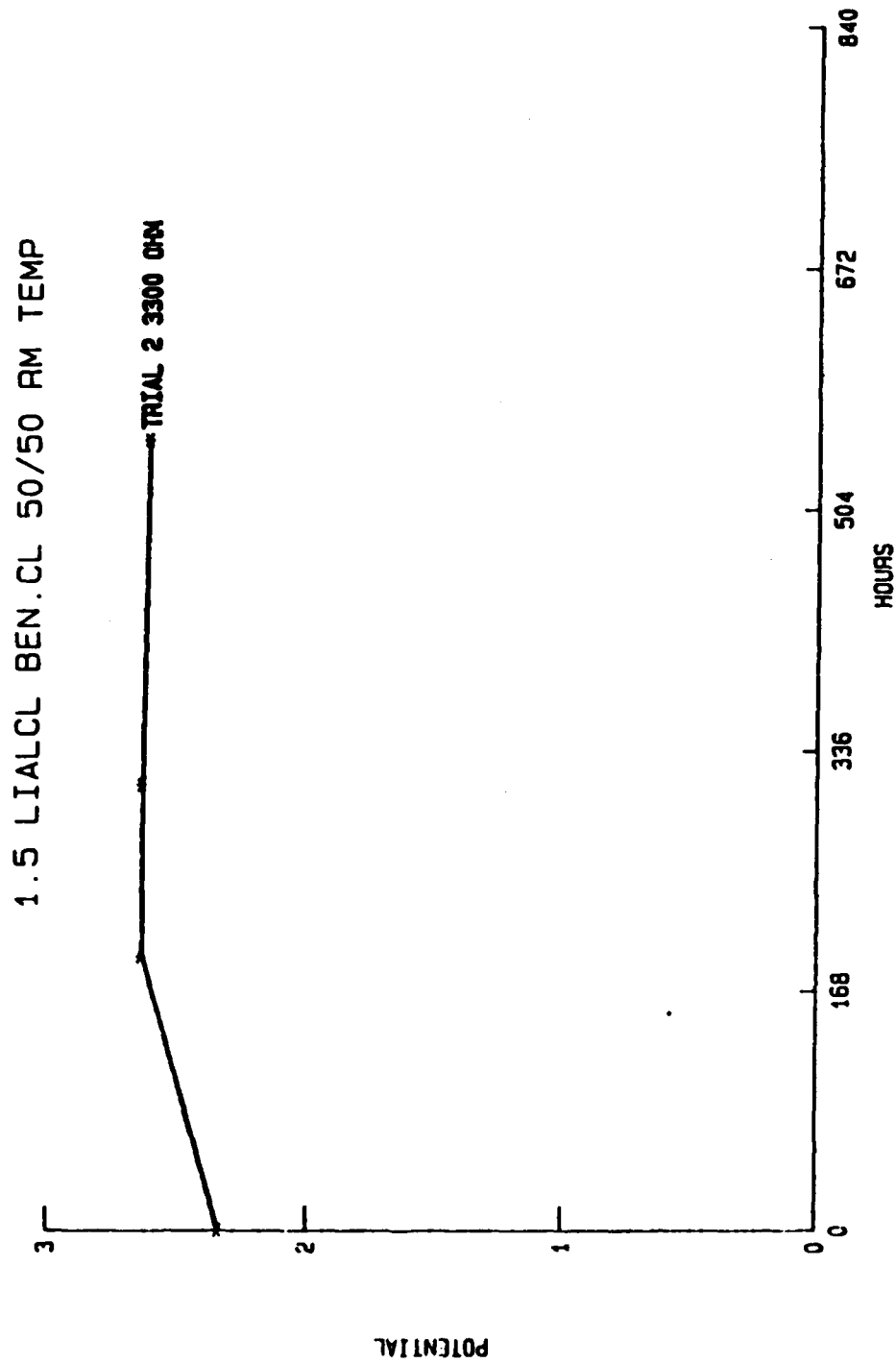


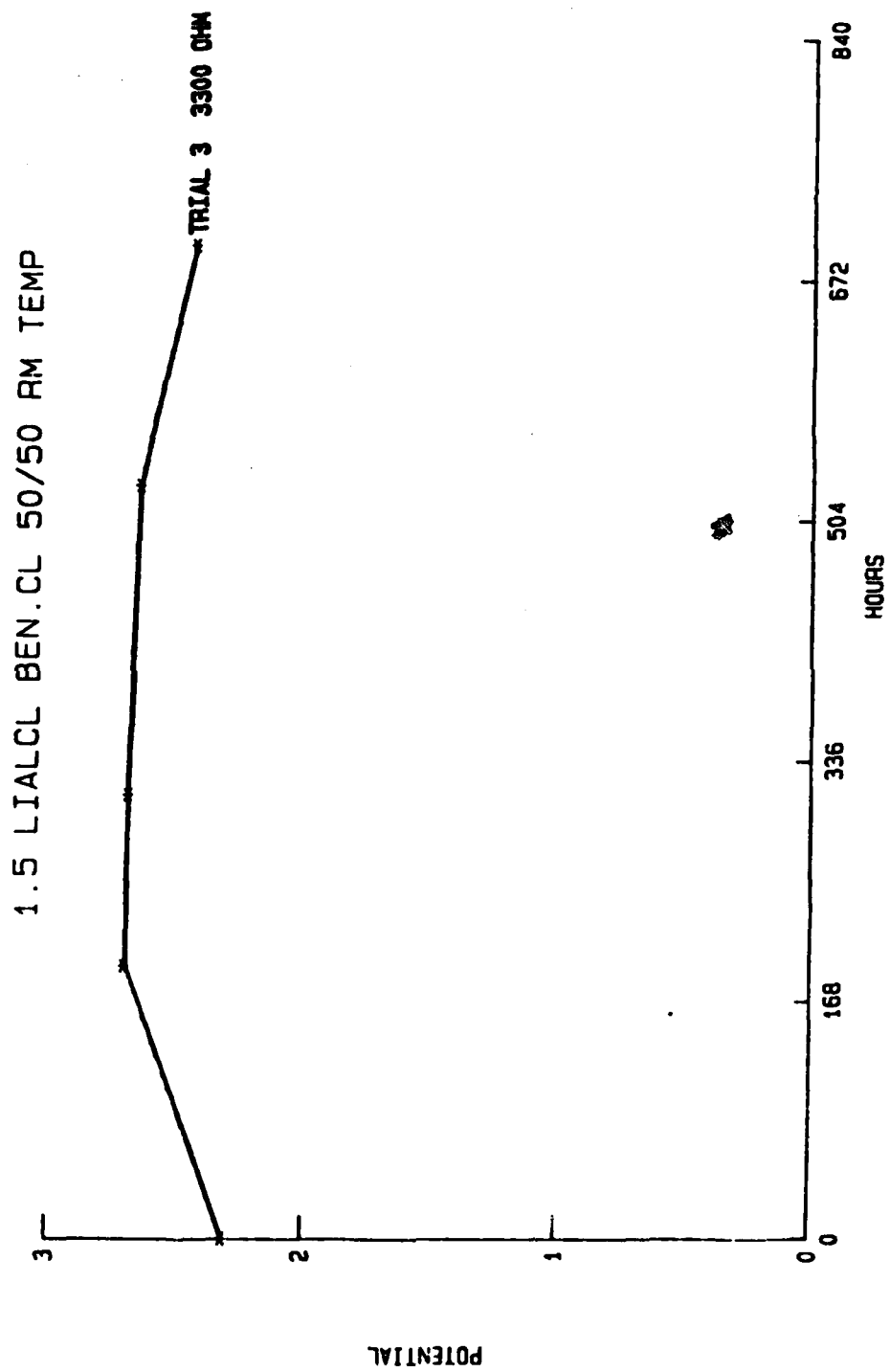
FIGURE 4 Galvanostatic Polarization of Calcium in $\text{Ca}(\text{AlCl}_4)_2 \text{SOCl}_2$ Electrolytes at Room Temperature

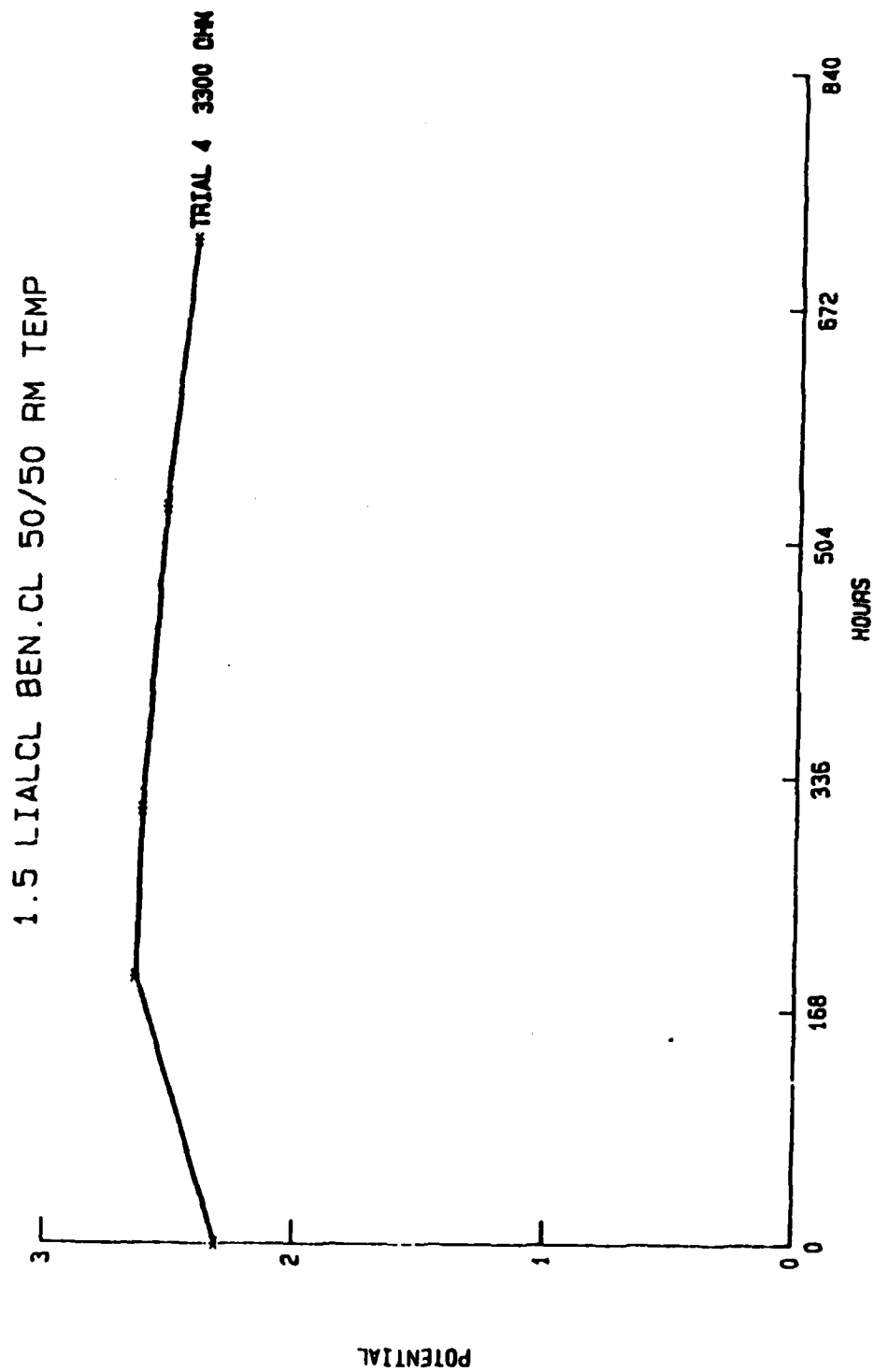
APPENDIX B

50/50 BENZOYL: THIONYL STORAGE MATRIX DISCHARGE CURVES

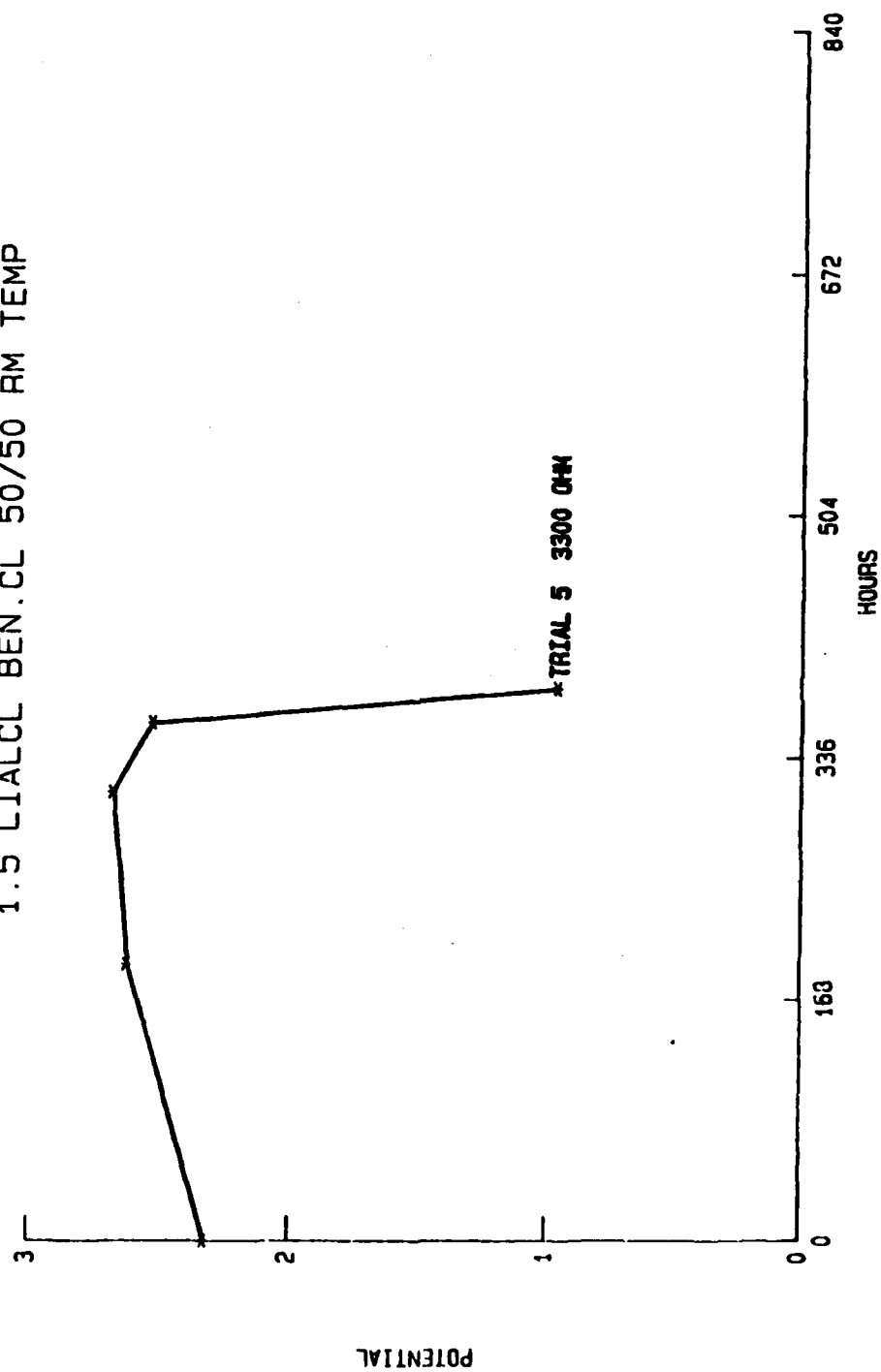




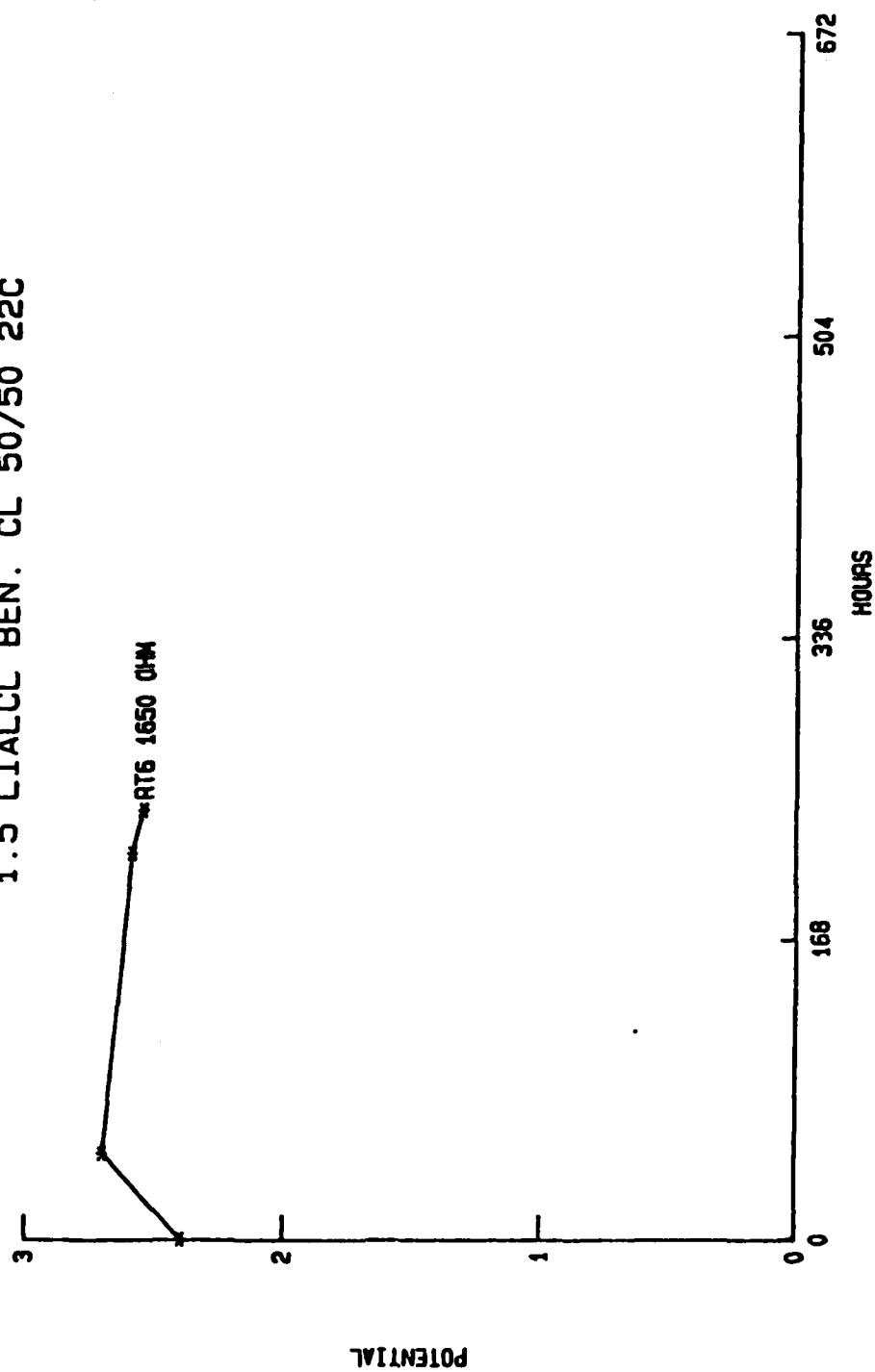




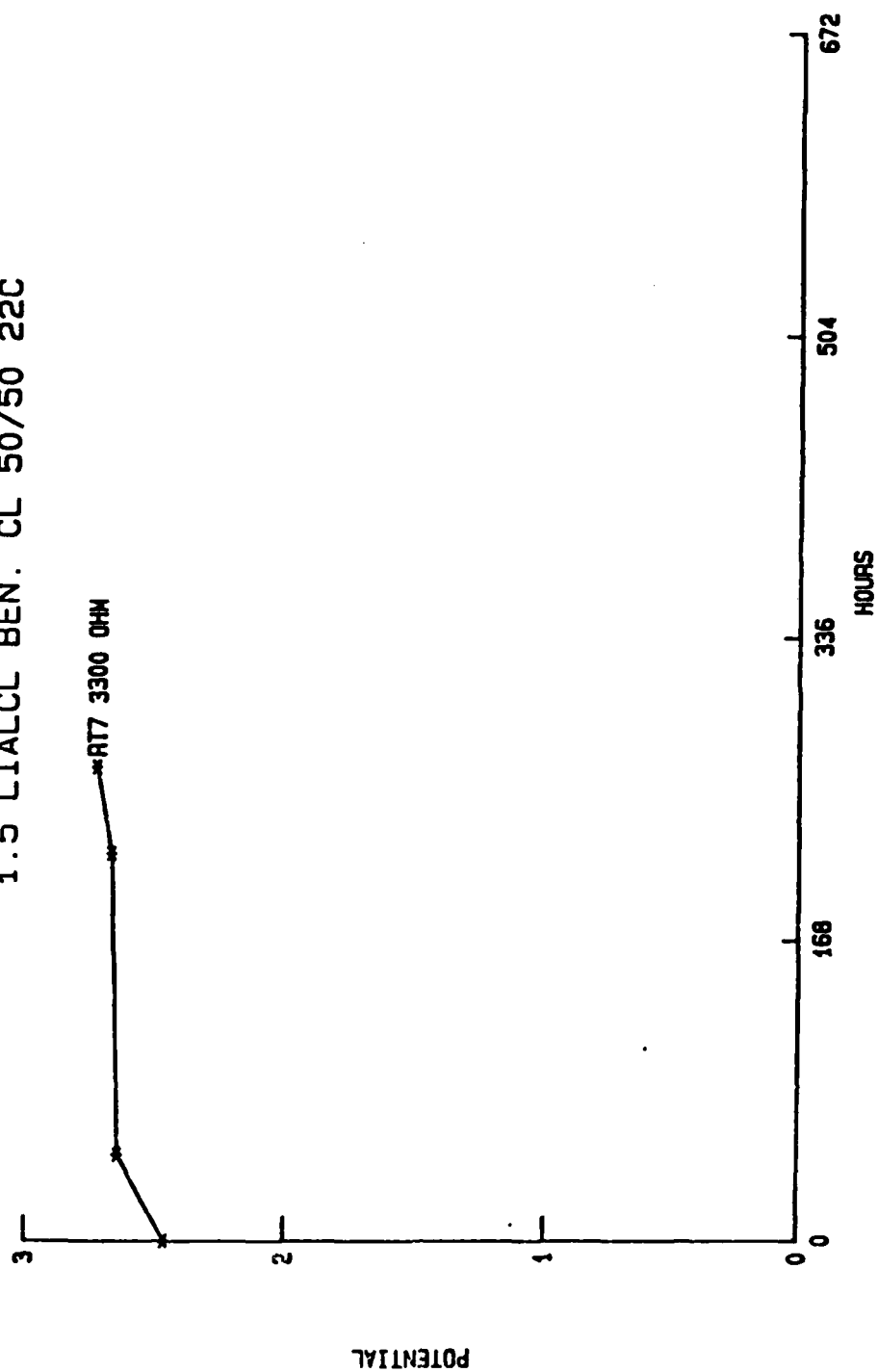
1.5 LIALCL BEN.CL 50/50 RM TEMP

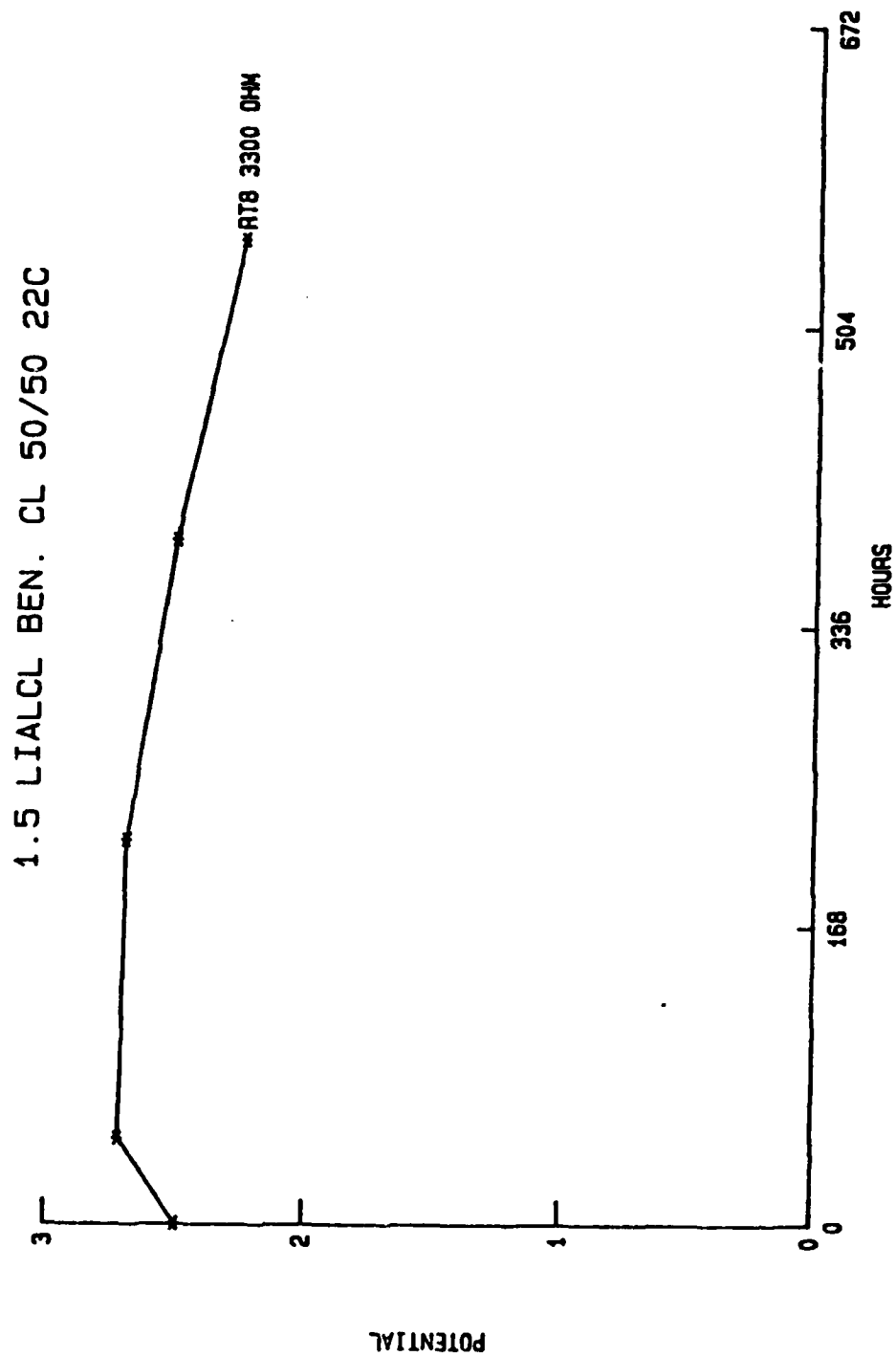


1.5 LIALCL BEN. CL 50/50 22C

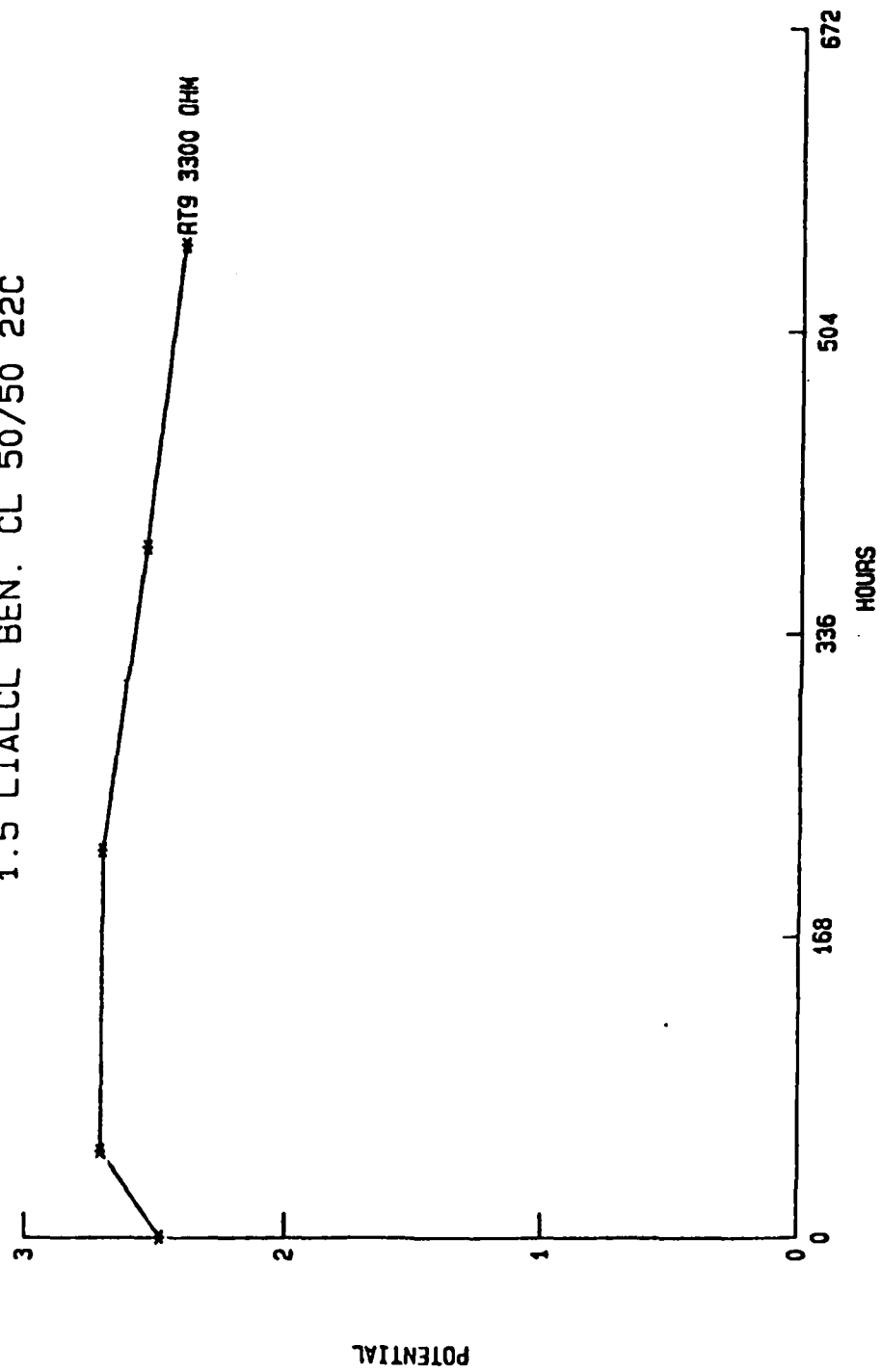


1.5 LIALCL BEN. CL 50/50 22C

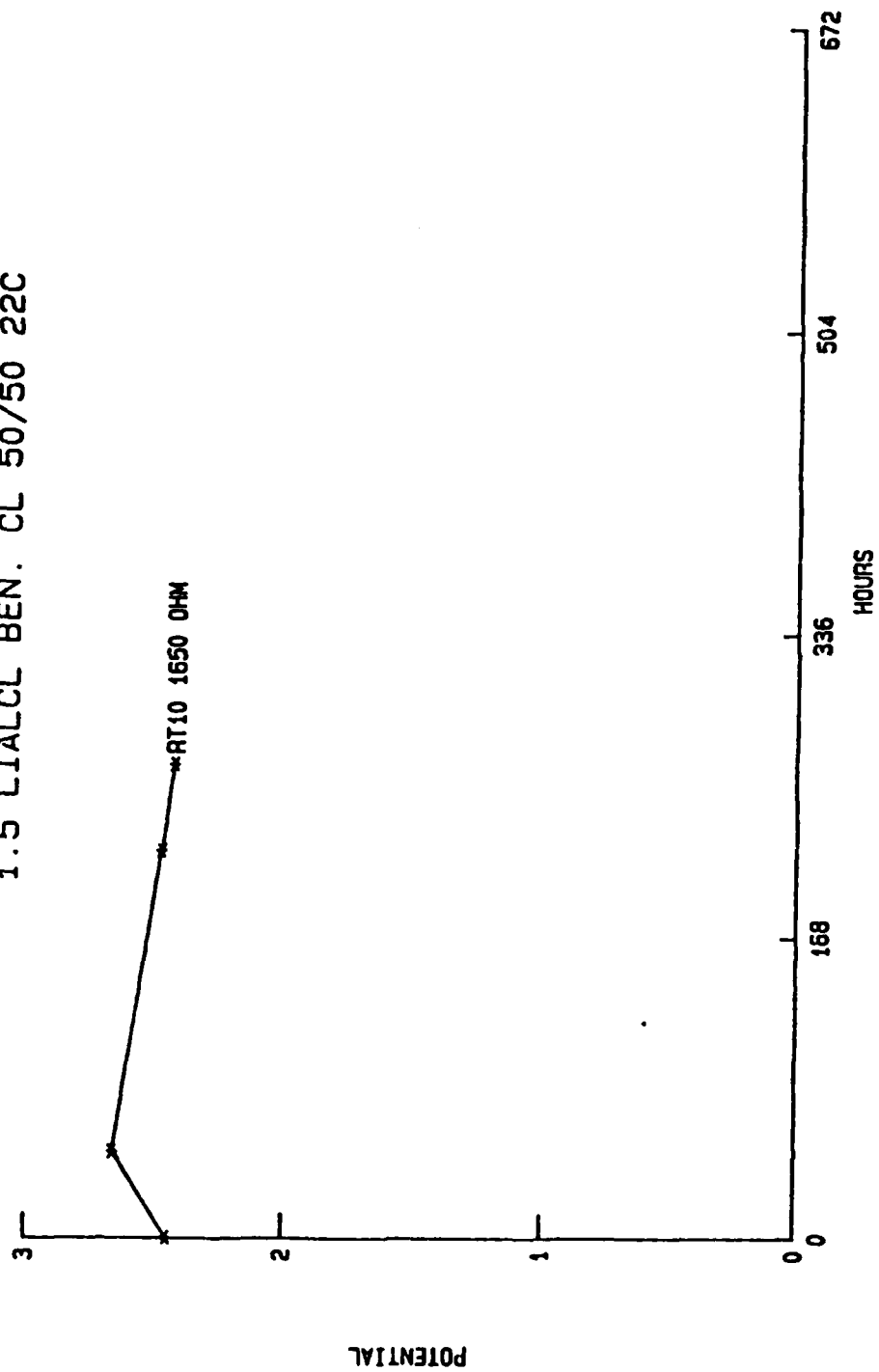




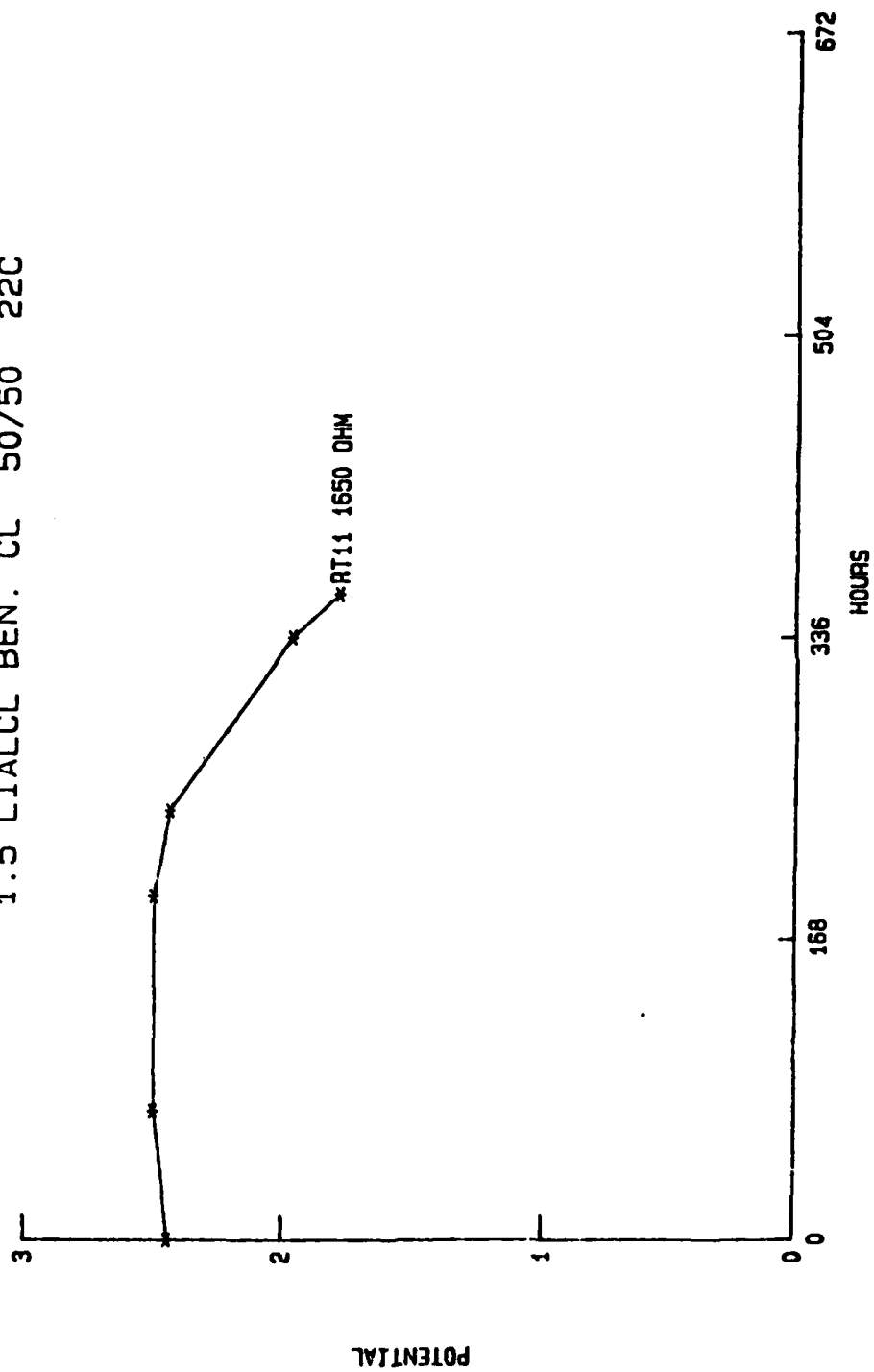
1.5 LIALCL BEN. CL 50/50 22C

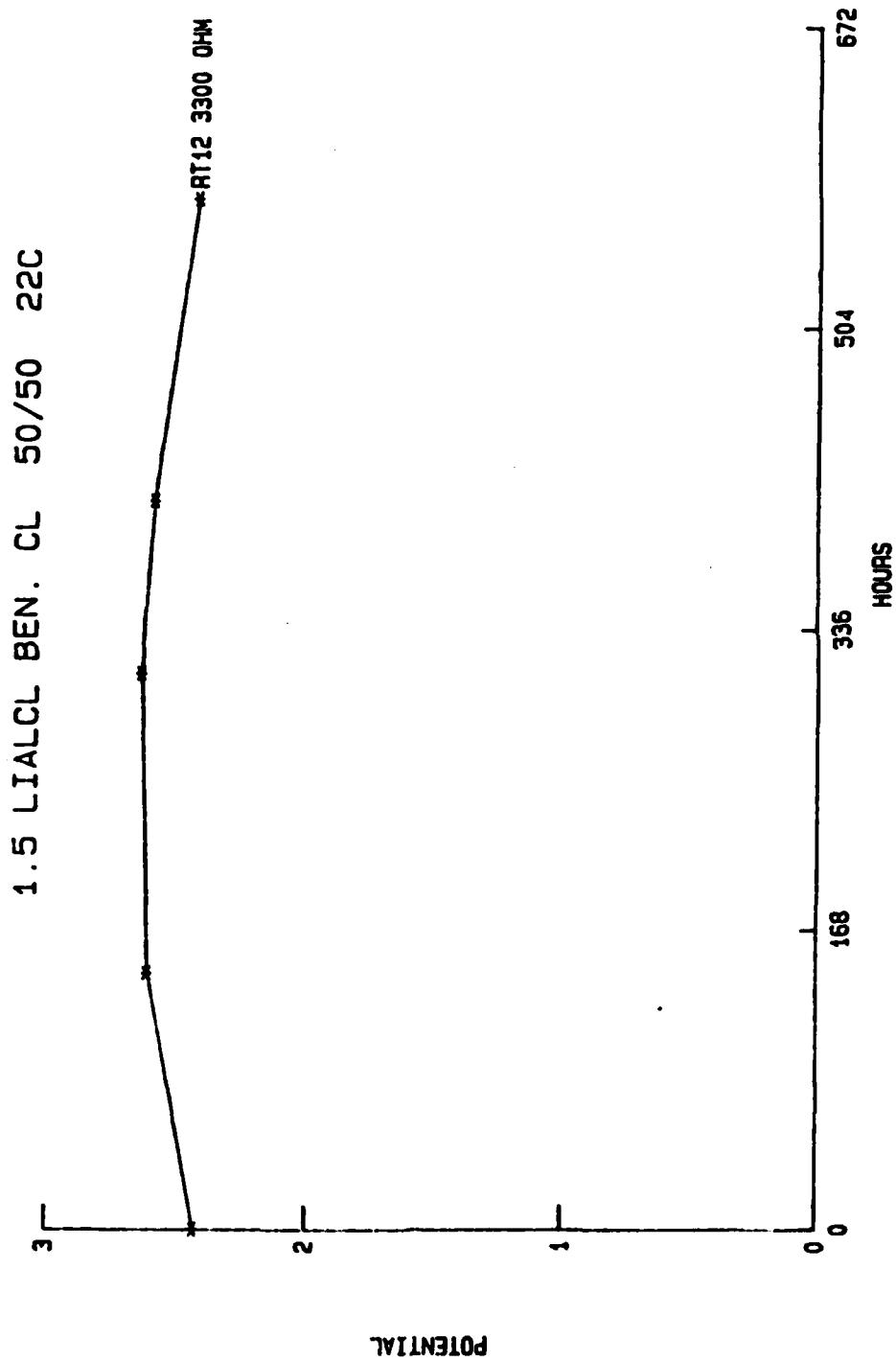


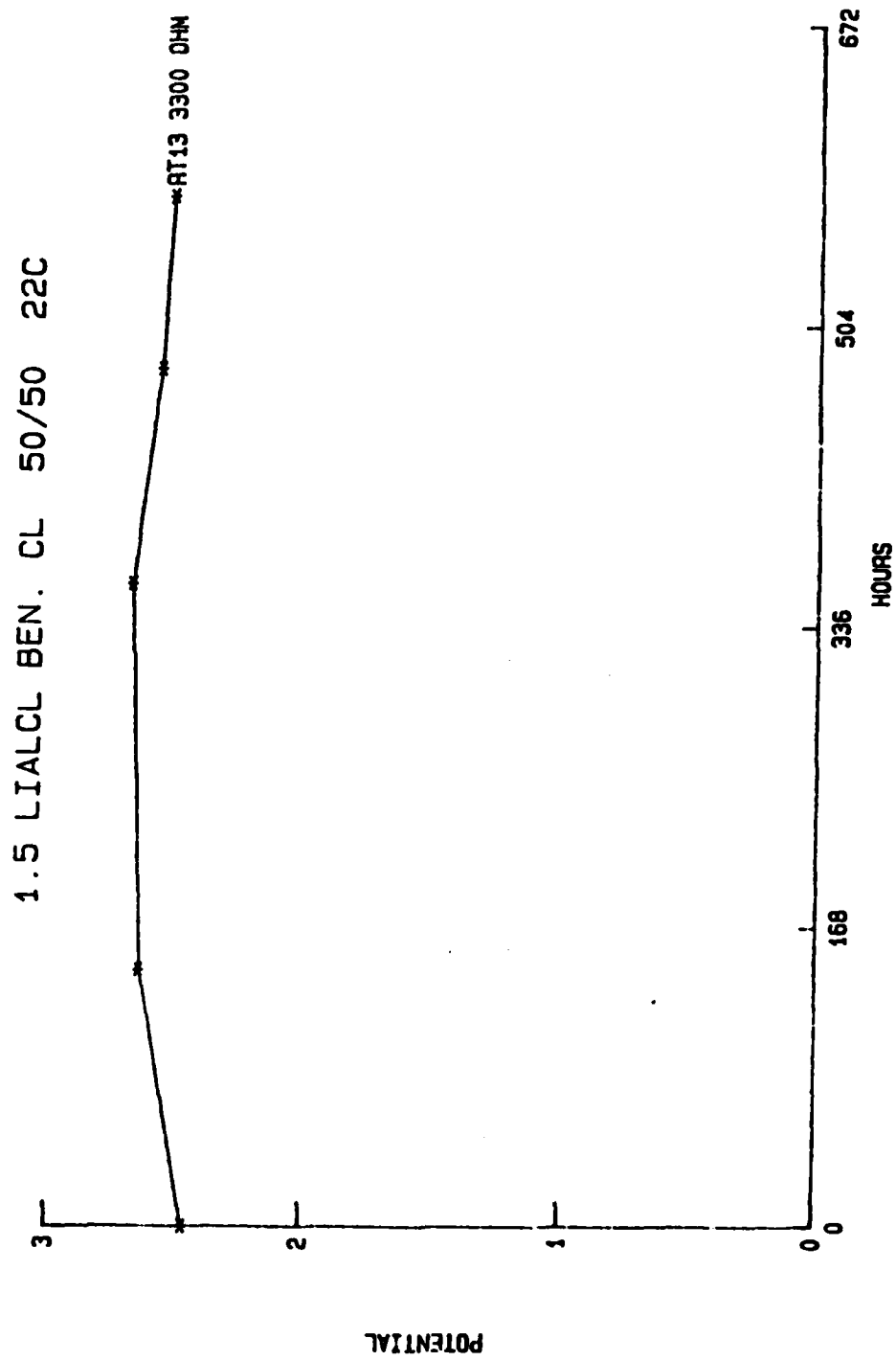
1.5 LIALCL BEN. CL 50/50 22C



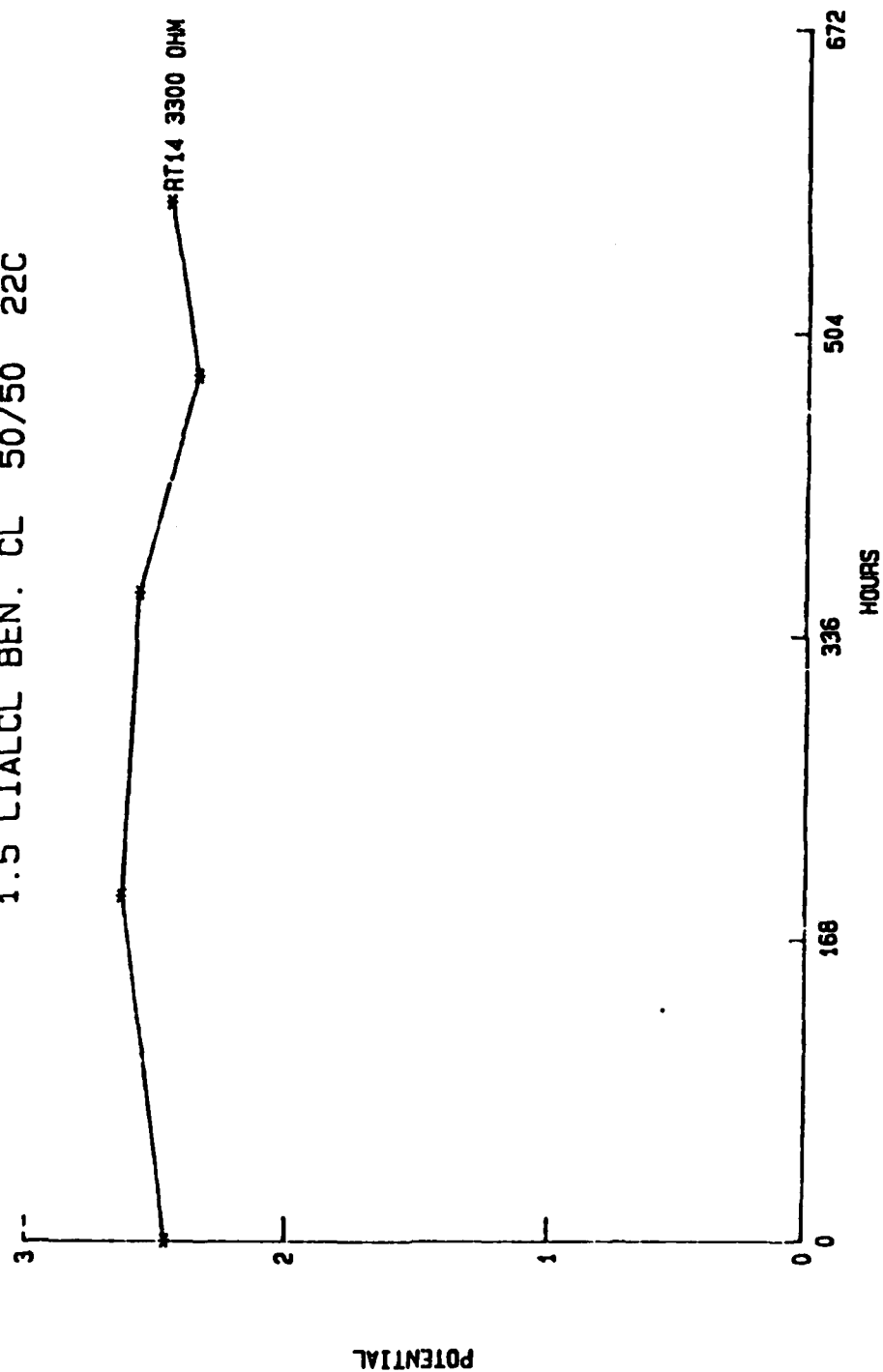
1.5 LIALCL BEN. CL 50/50 22C



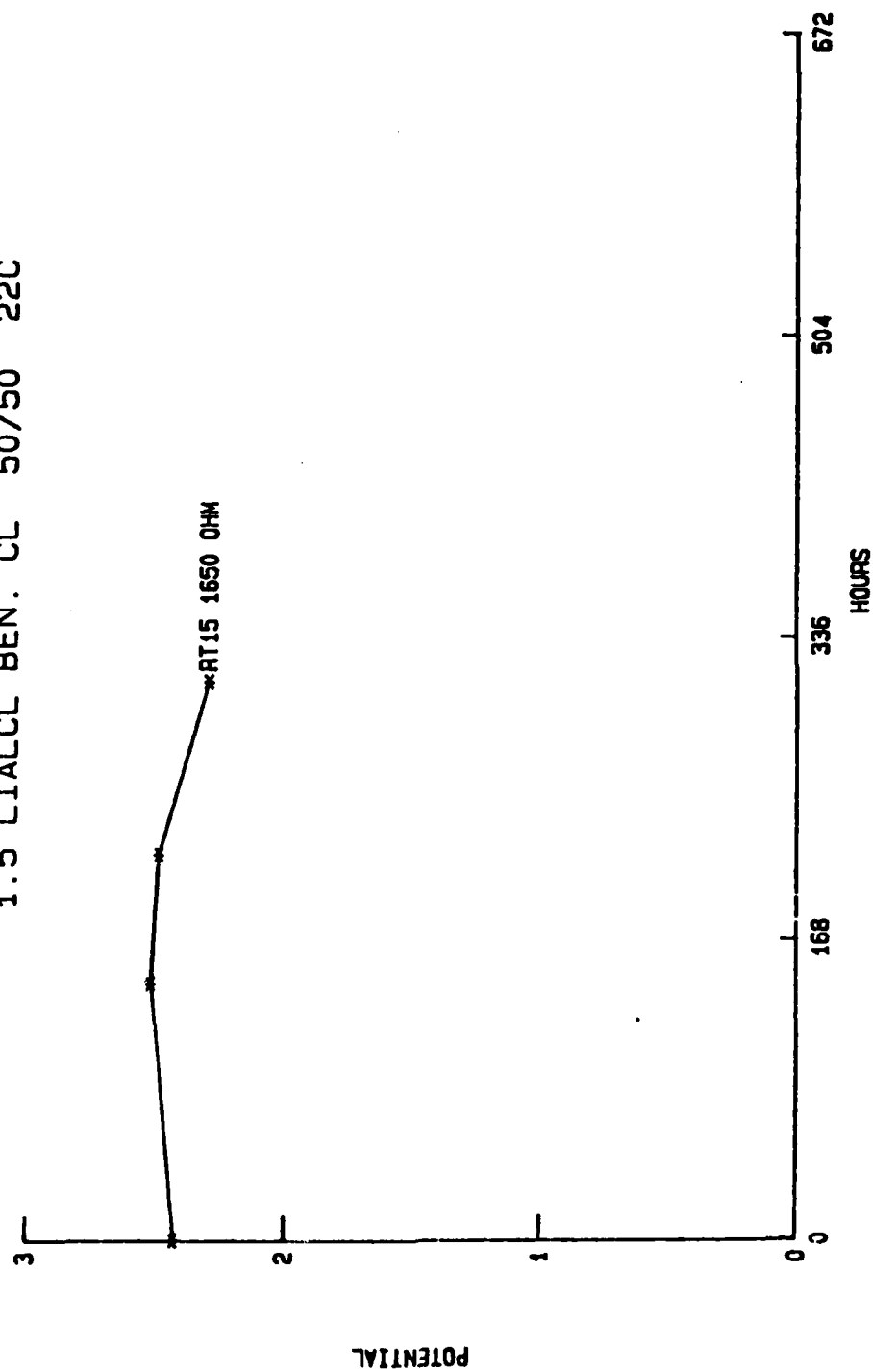




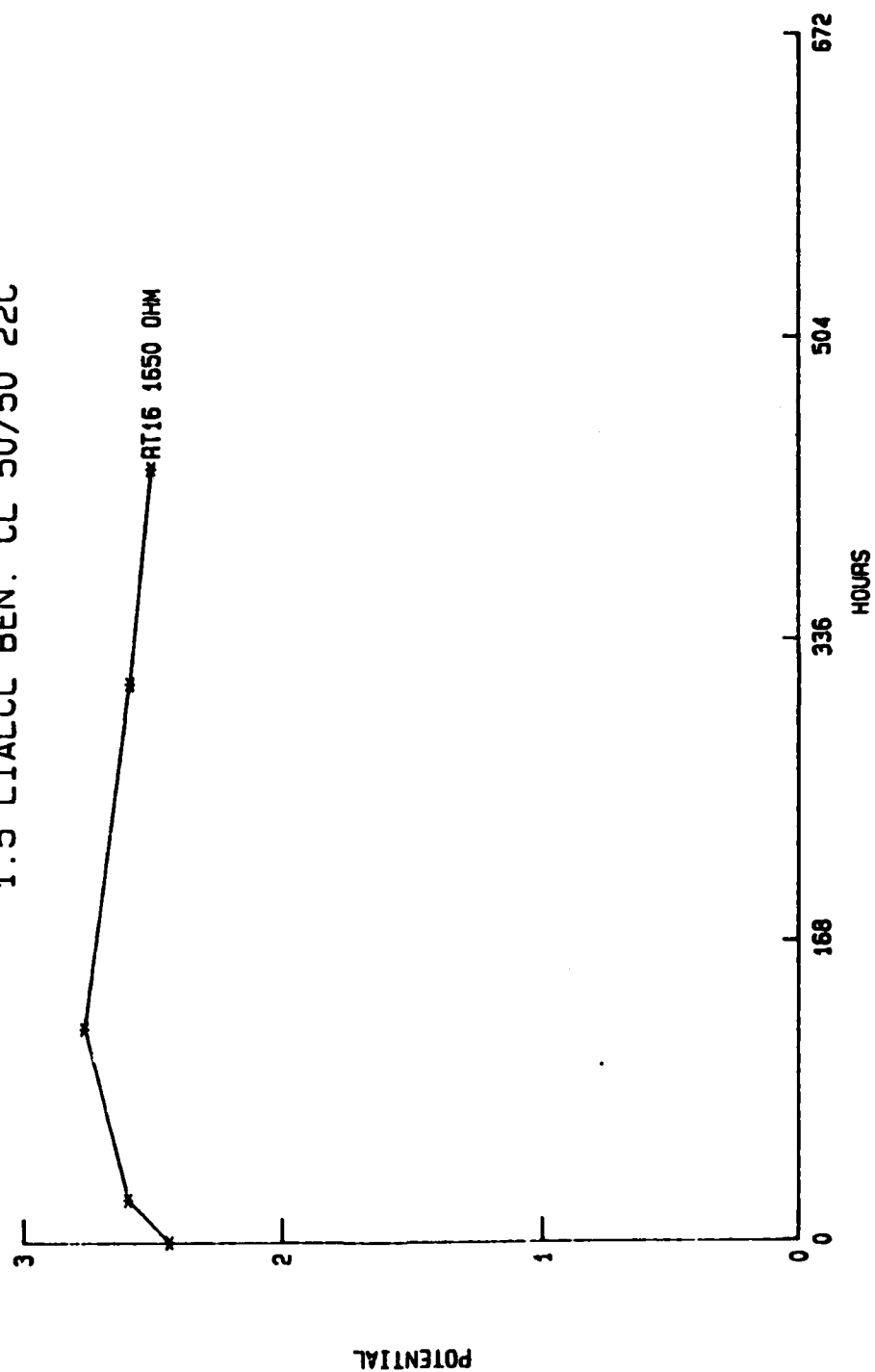
1.5 LIALCL BEN. CL 50/50 22C



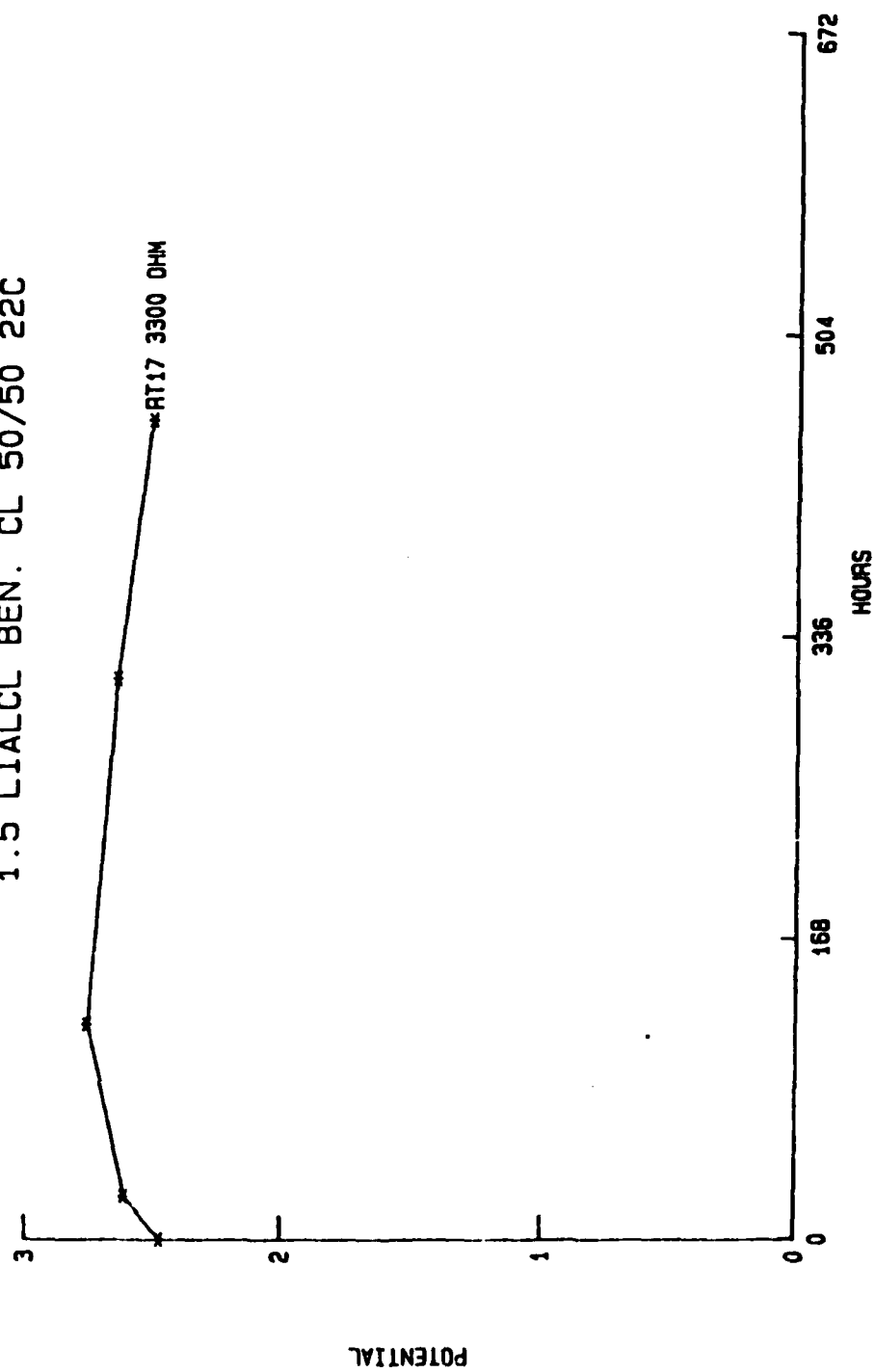
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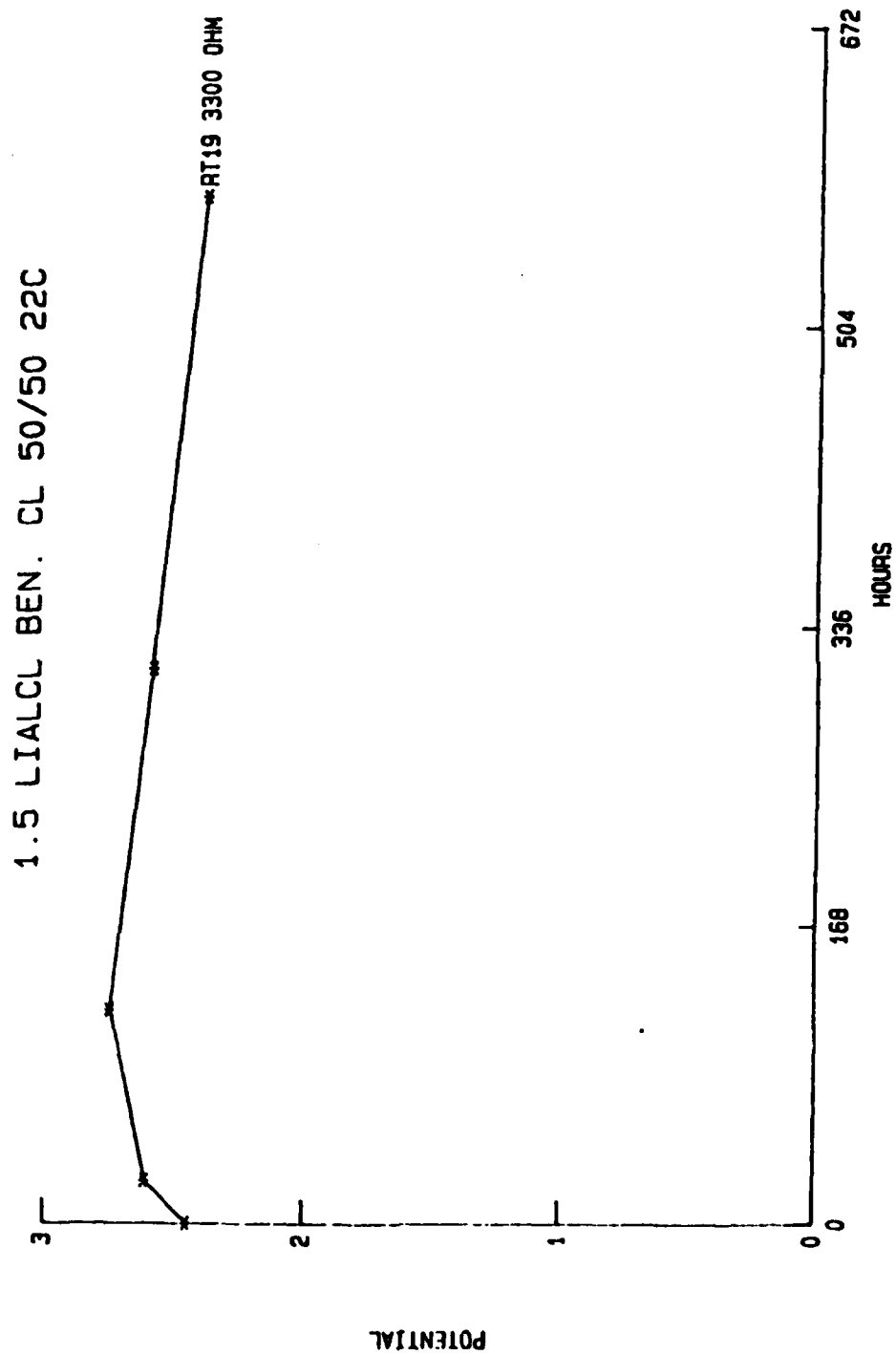


1.5 LIALCL BEN. CL 50/50 22C

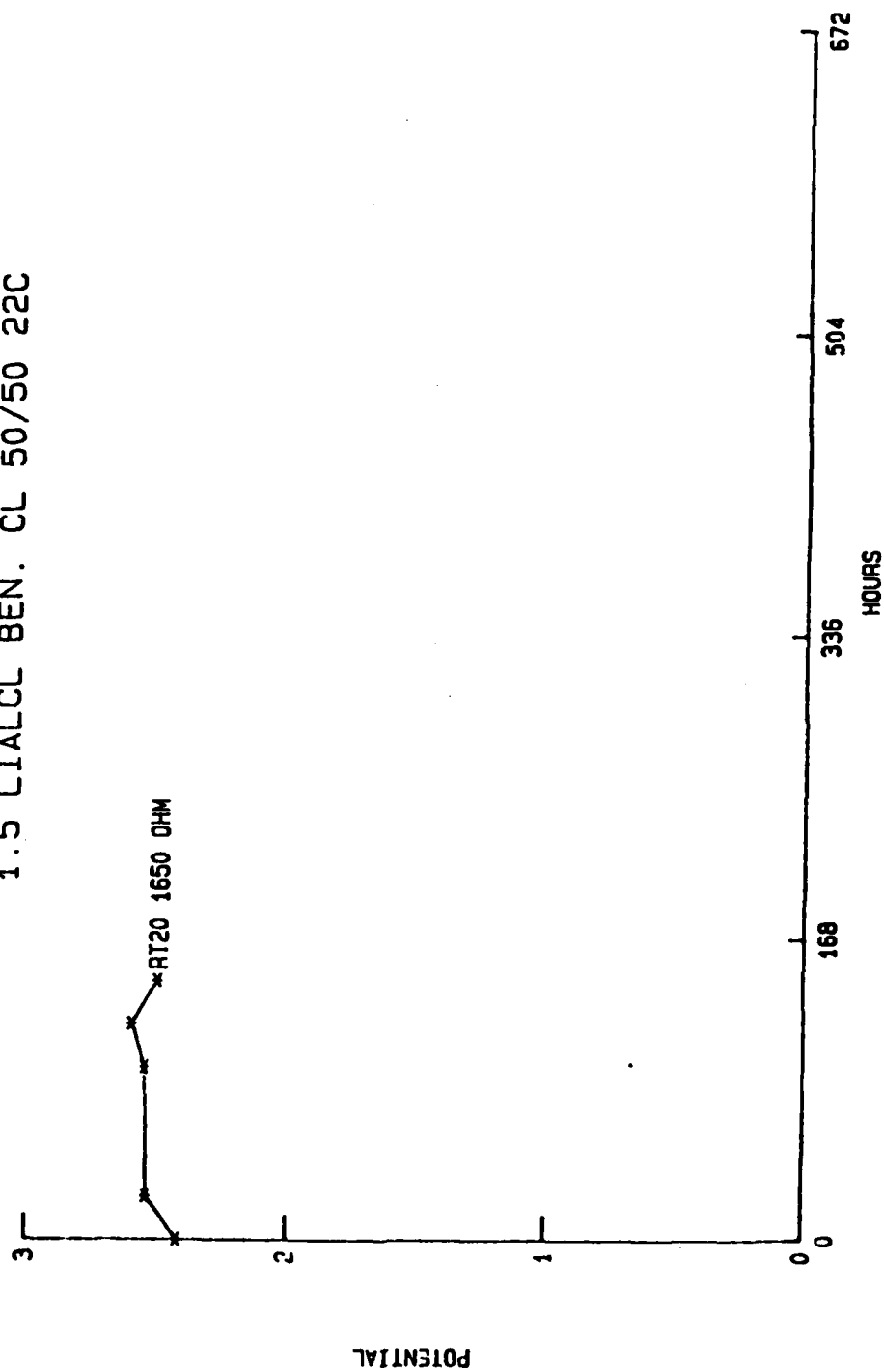


1.5 LIALCL BEN. CL 50/50 22C

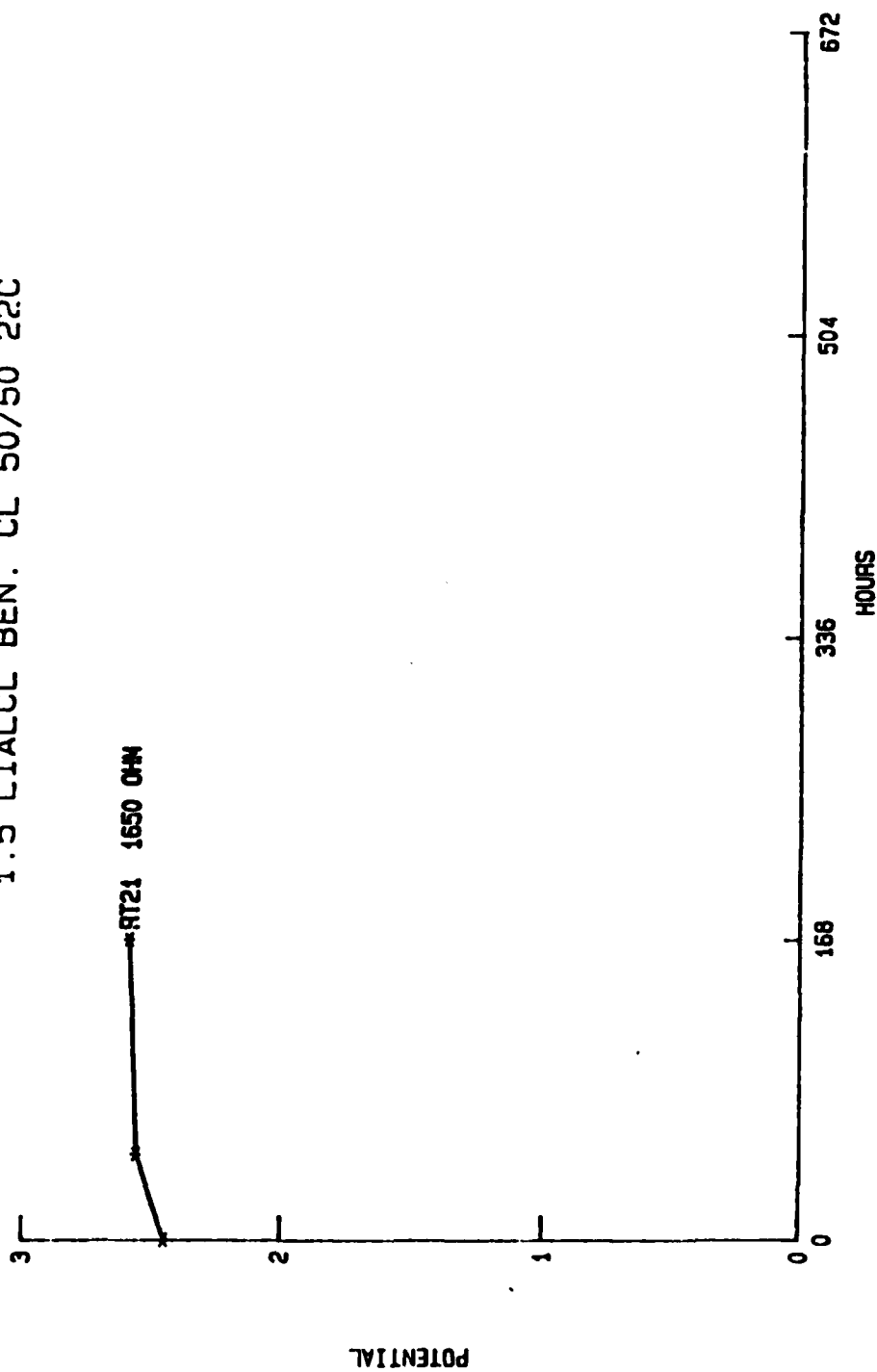




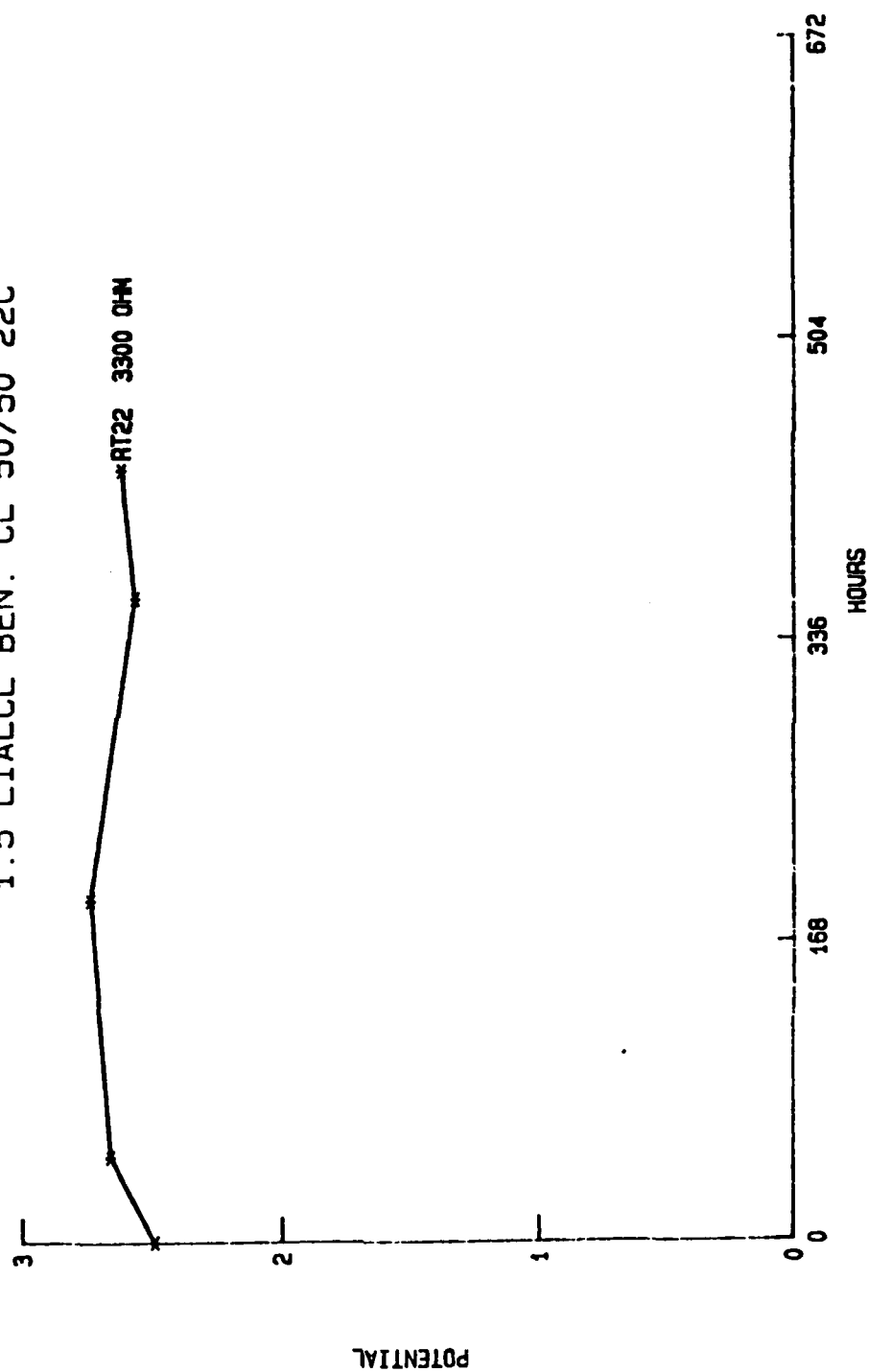
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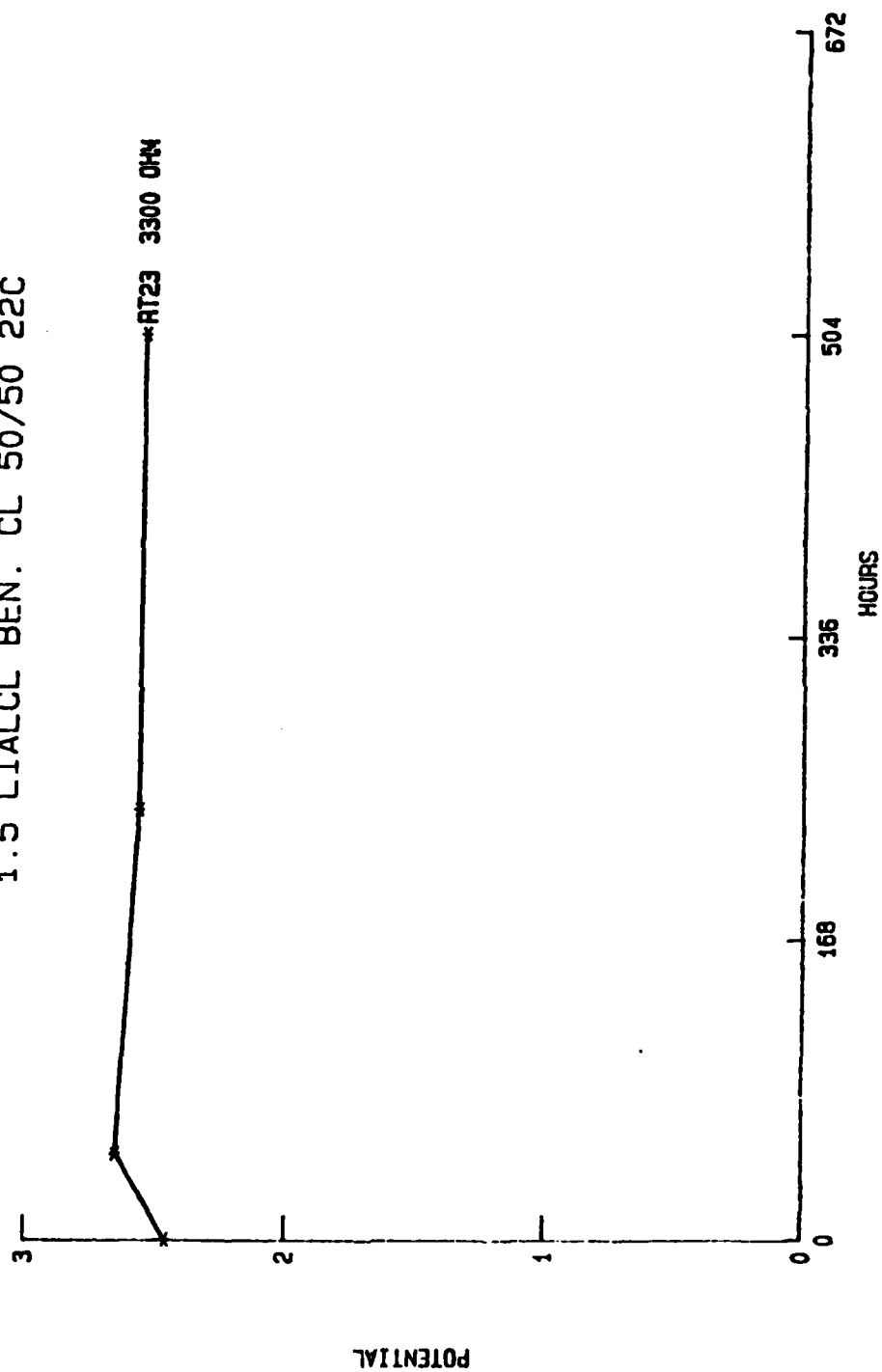
1.5 LIALCL BEN. CL 50/50 22C

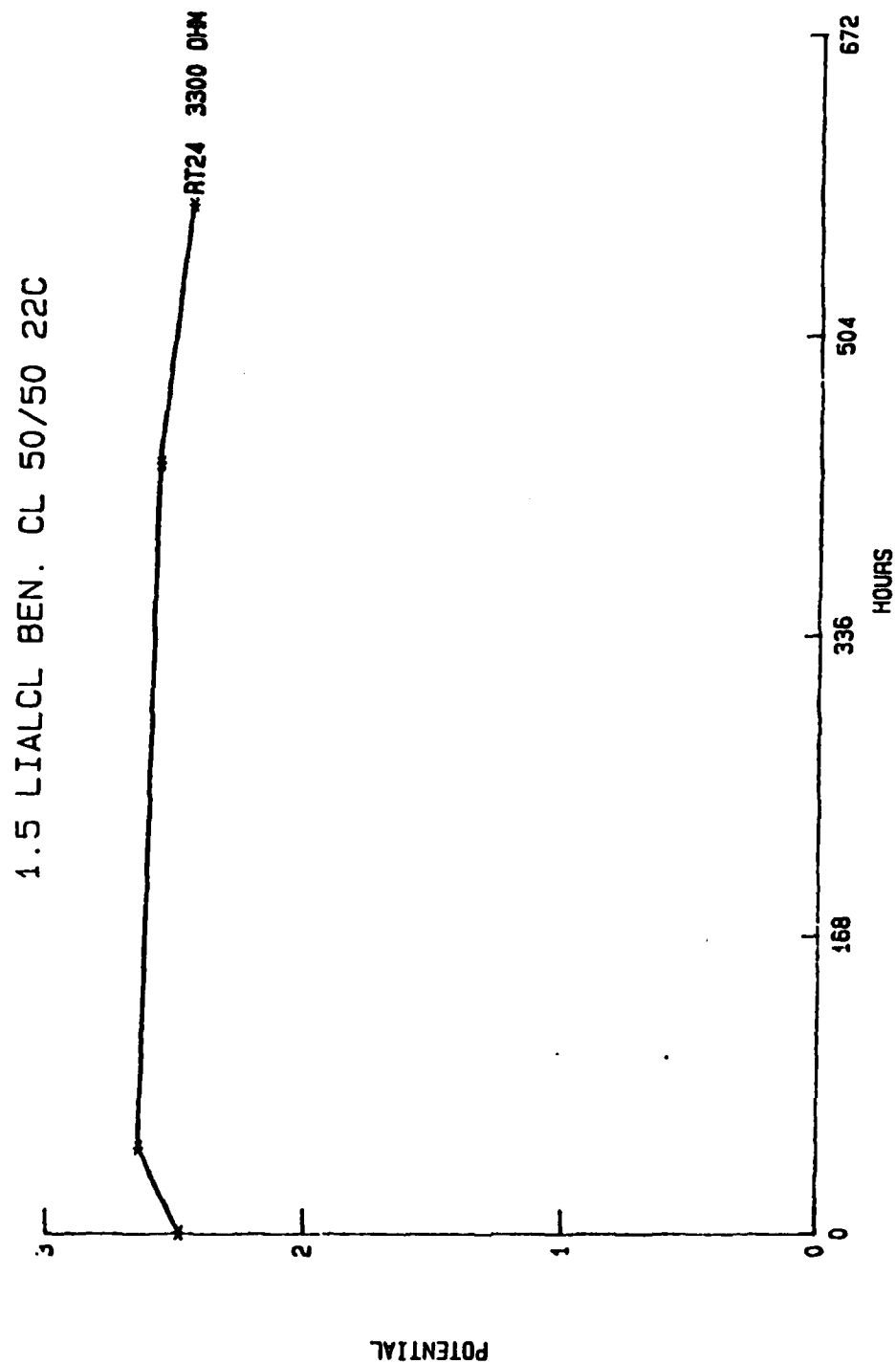


1.5 LIALCL BEN. CL 50/50 22C

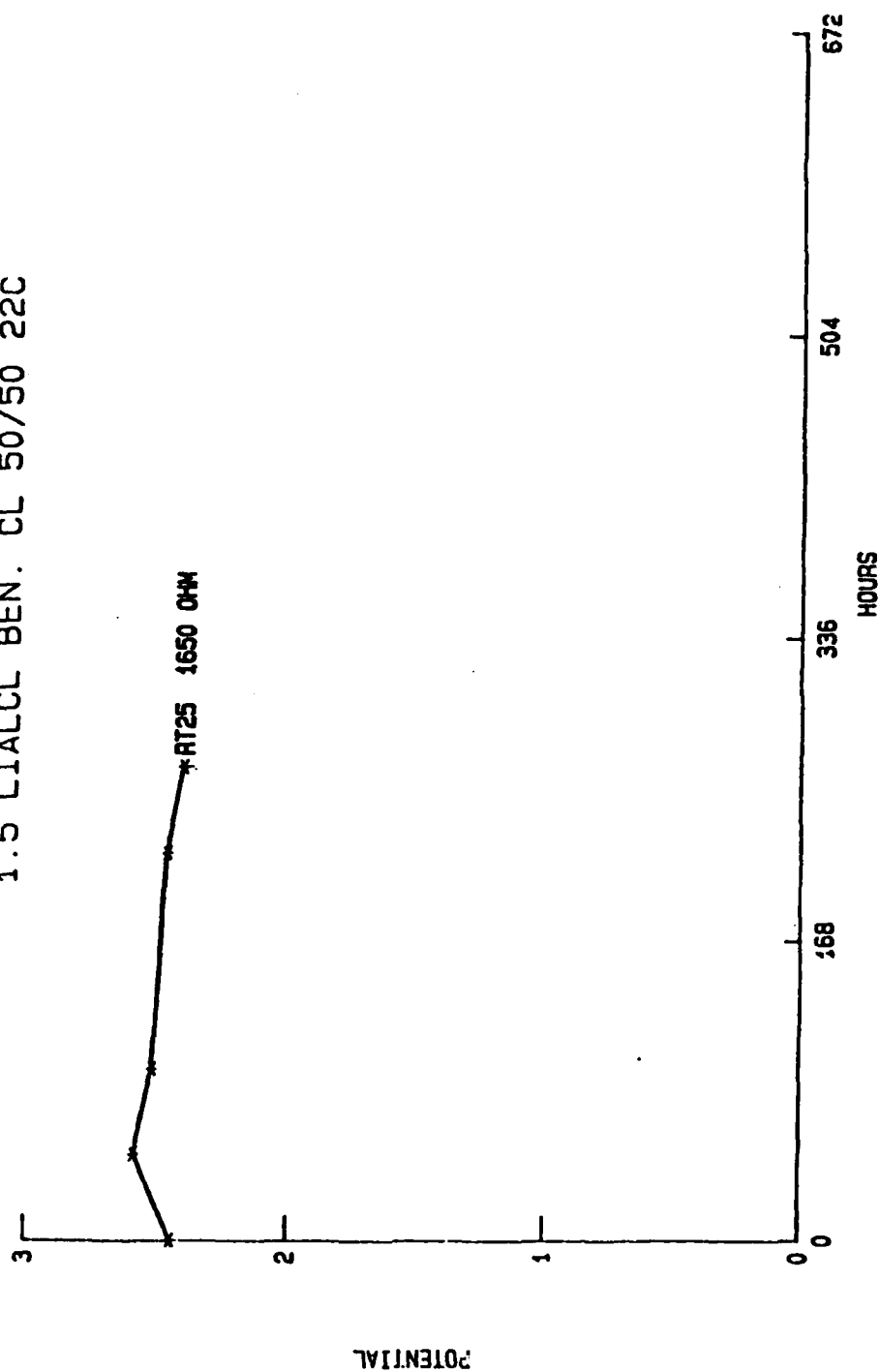


1.5 LIALCL BEN. CL 50/50 22C

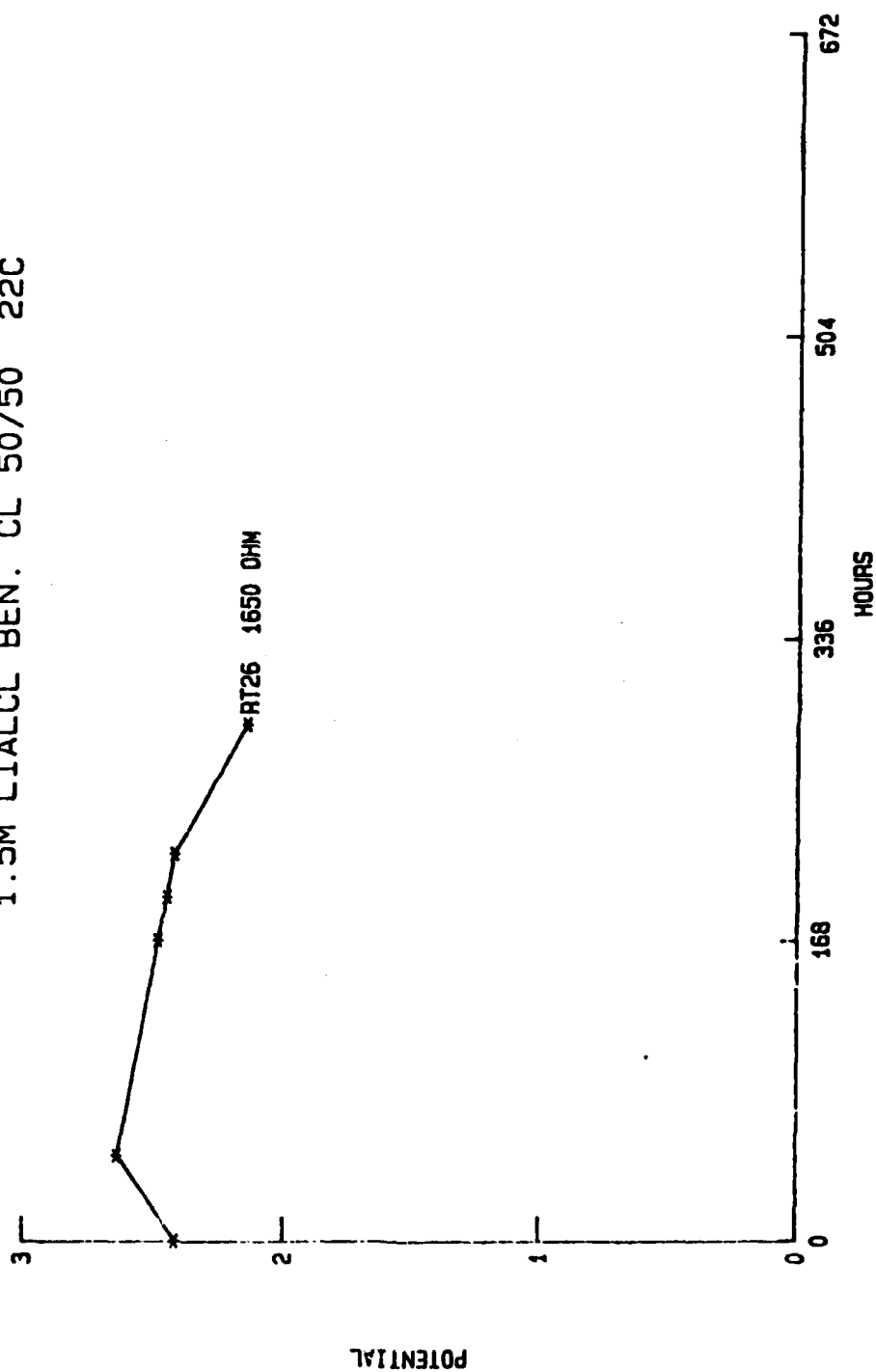


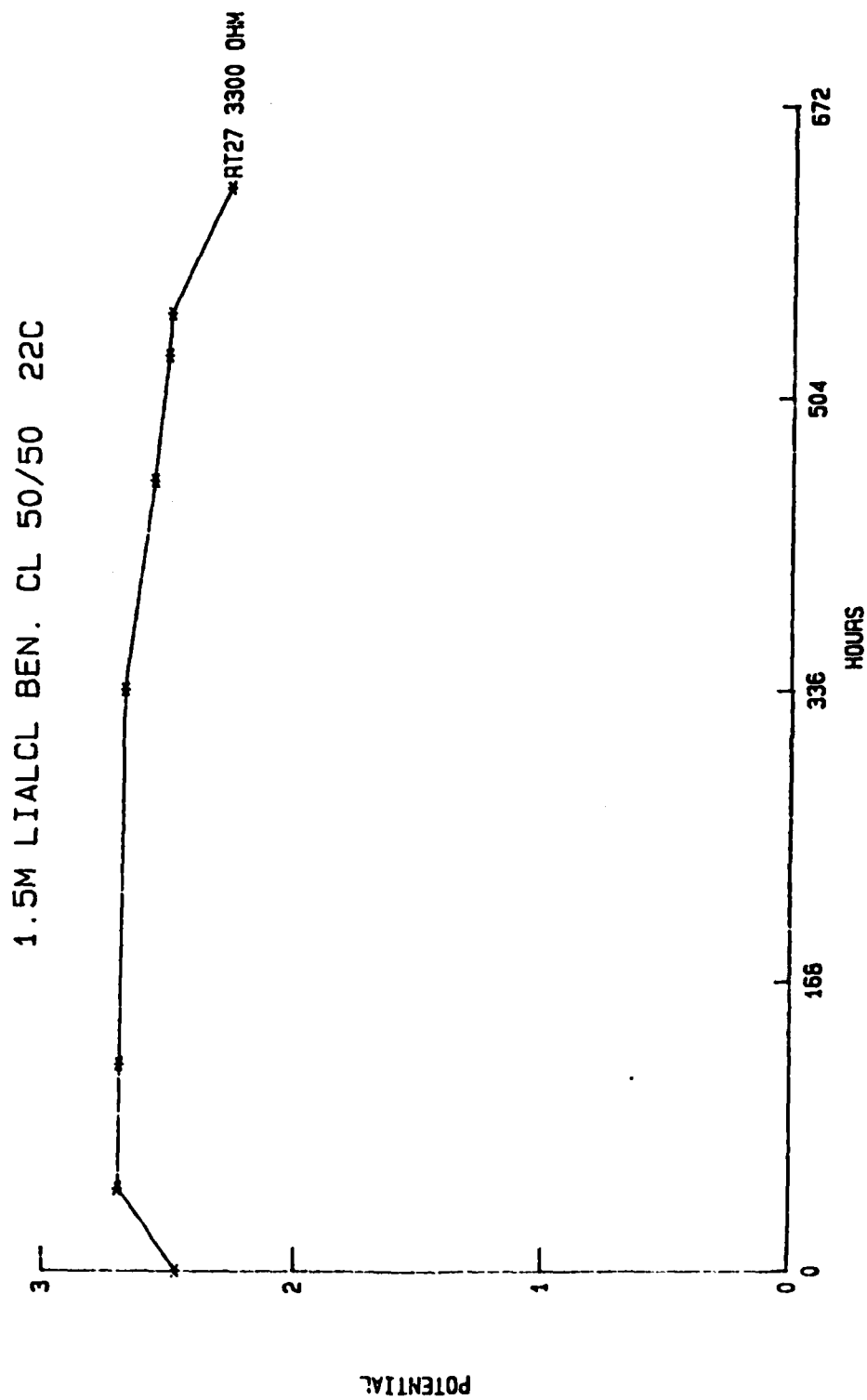


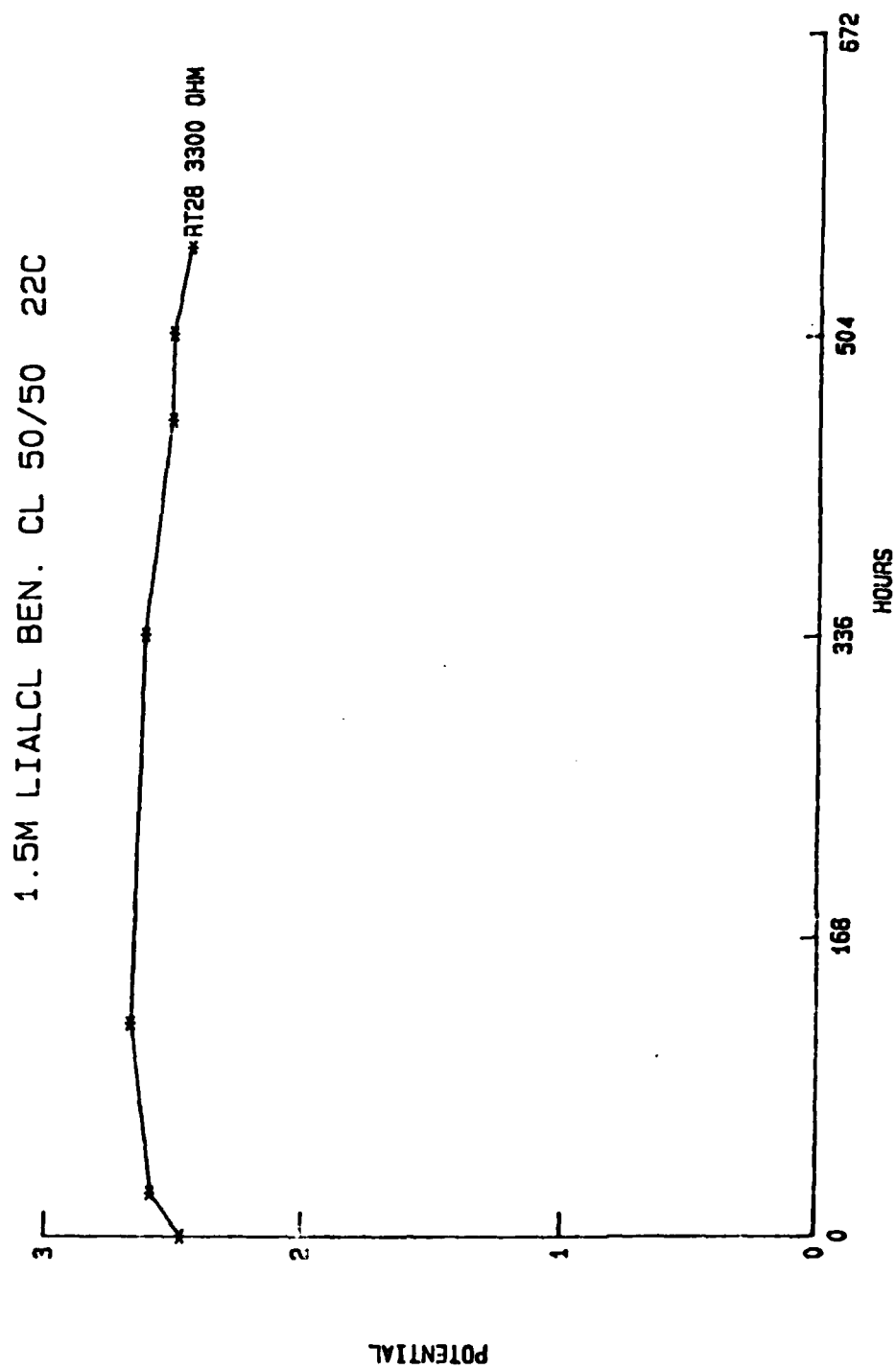
1.5 LIALCL BEN. CL 50/50 22C



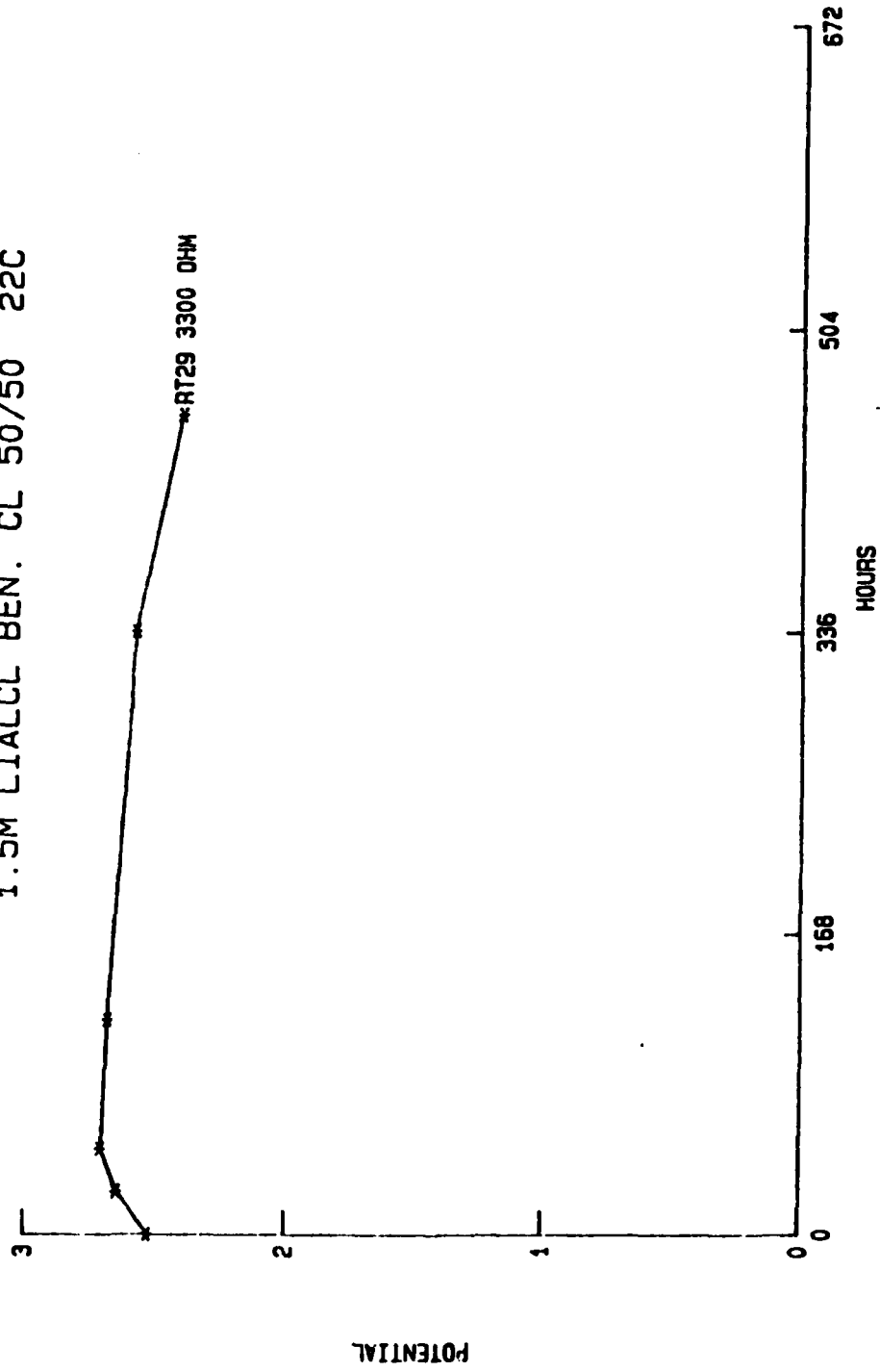
1.5M LIALCL BEN. CL 50/50 22C



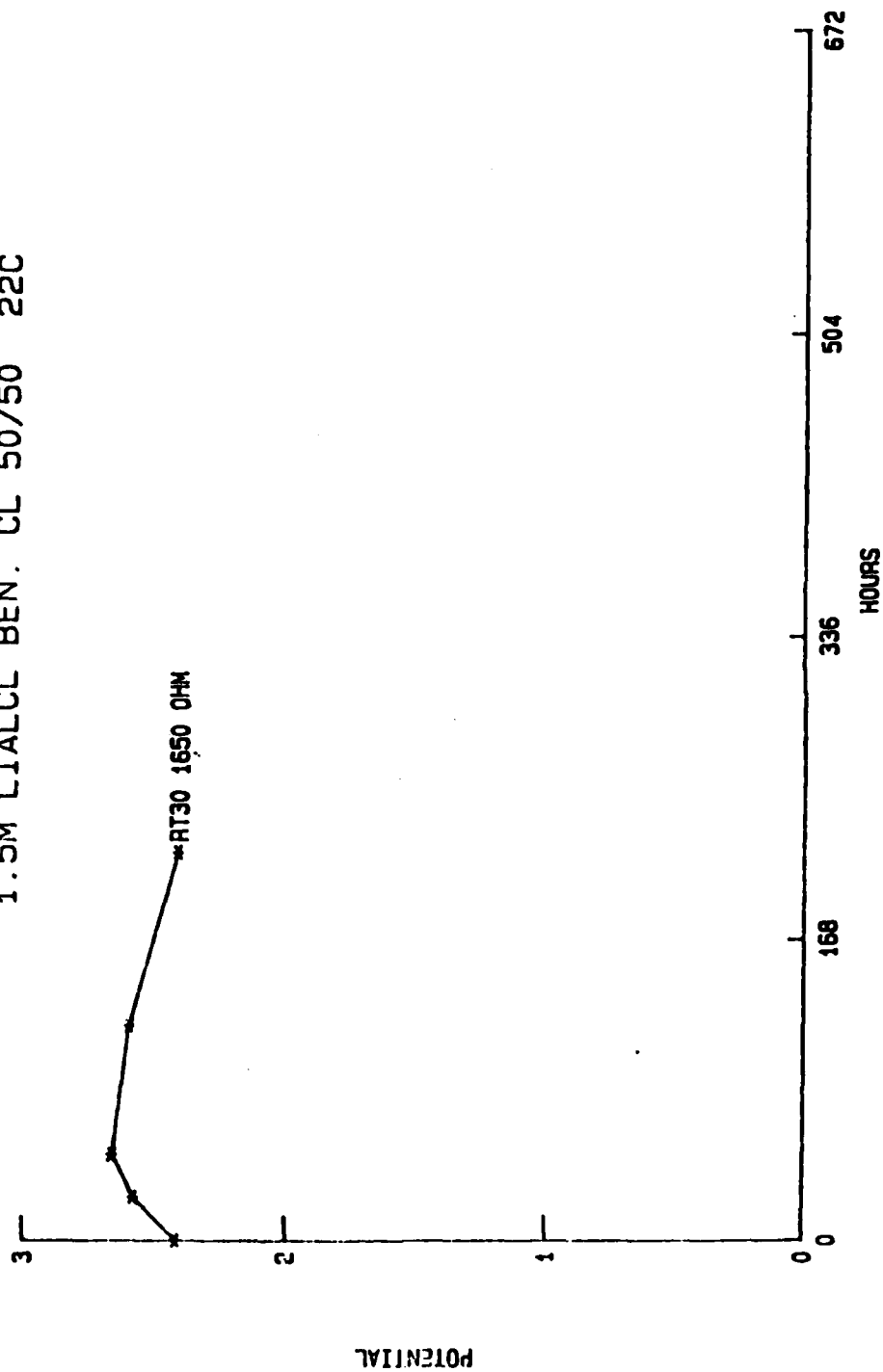




1.5M LIALCL BEN. CL 50/50 22C



1.5M LIALCL BEN. CL 50/50 22C

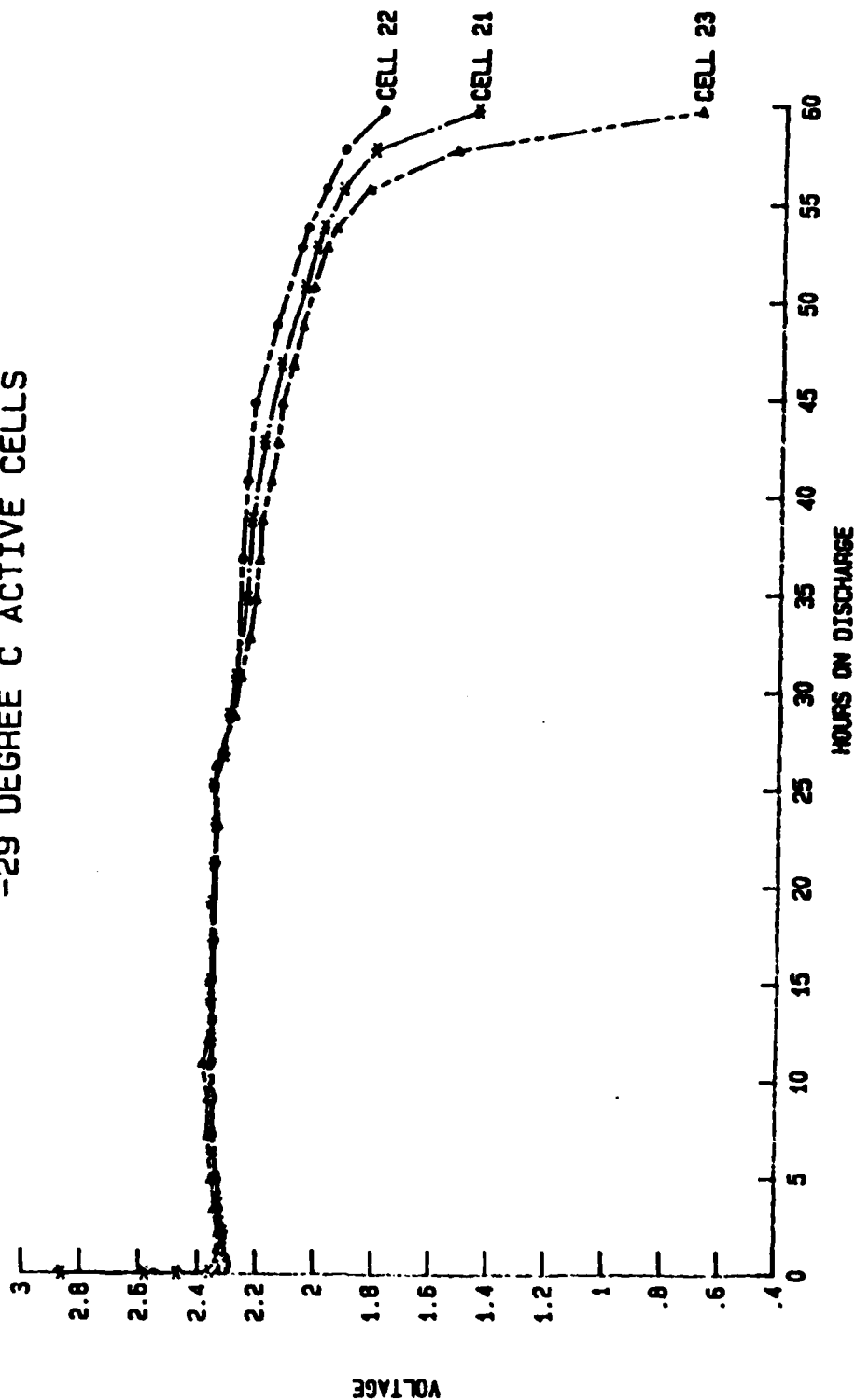


APPENDIX C

PROOF-OF-CONCEPT ACTIVE CELL DISCHARGE CURVES

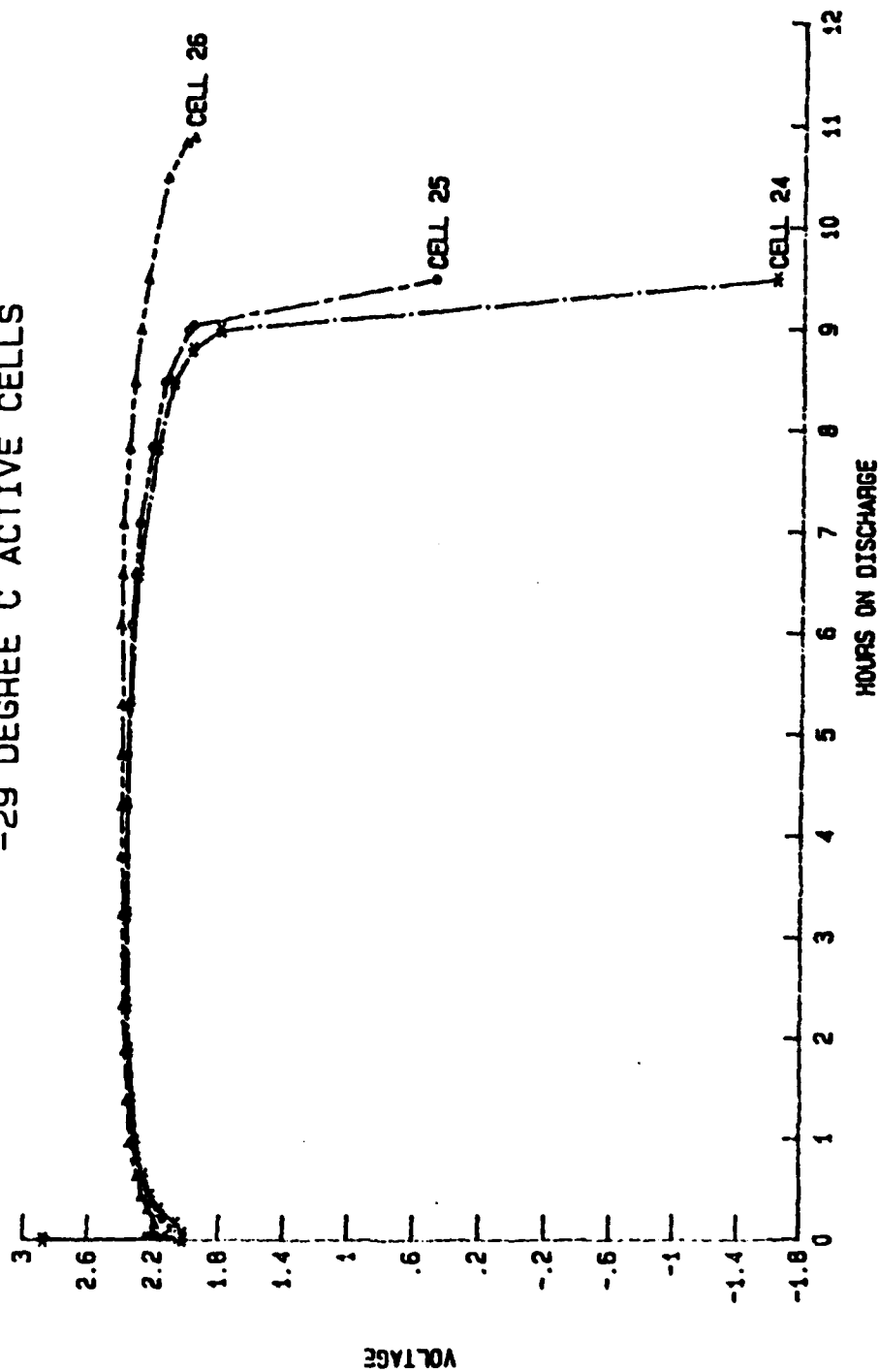
CA/SOCL2 80 MA DISCHARGE

-29 DEGREE C ACTIVE CELLS



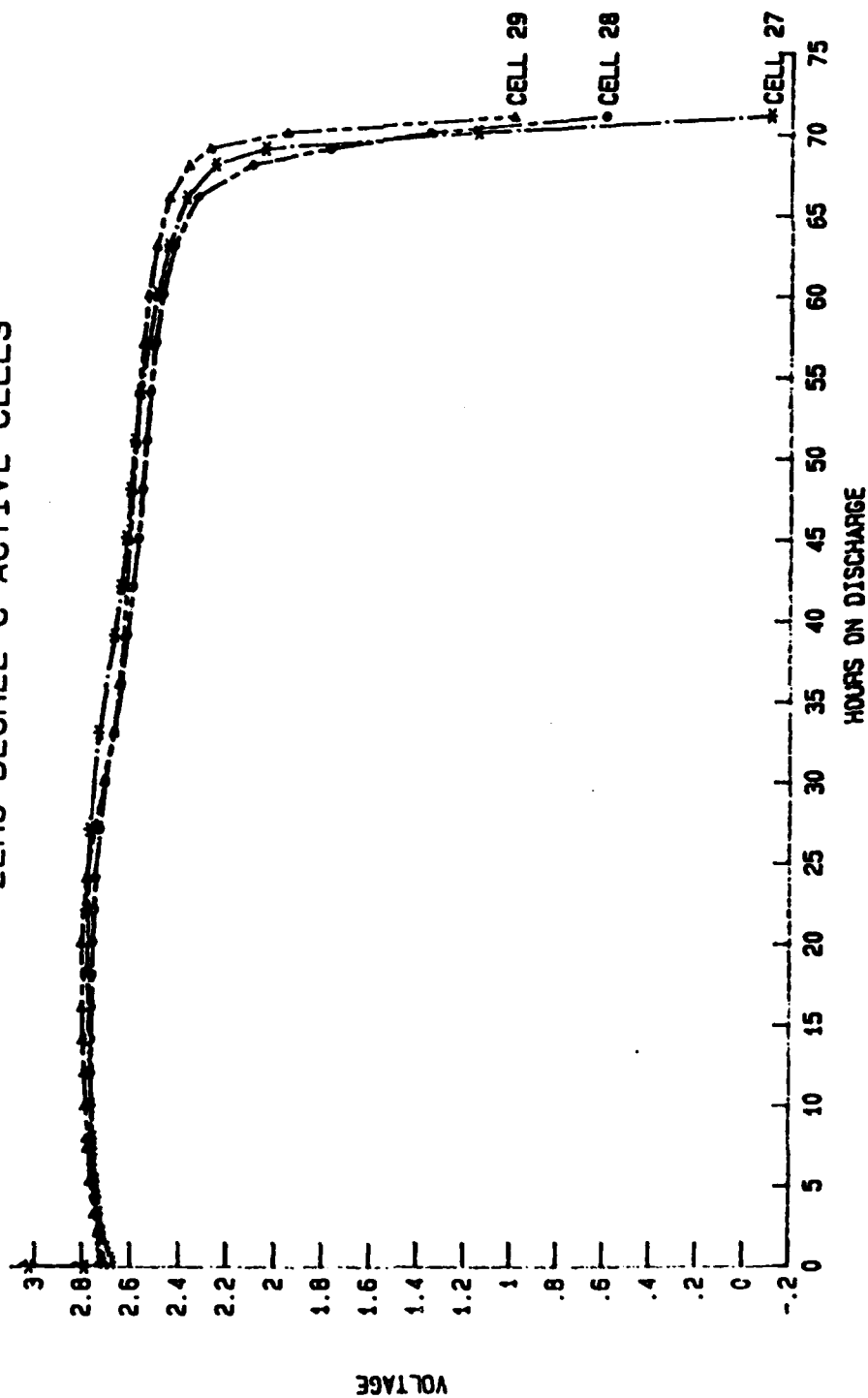
CA/SOCL2 400 MA DISCHARGE

-29 DEGREE C ACTIVE CELLS



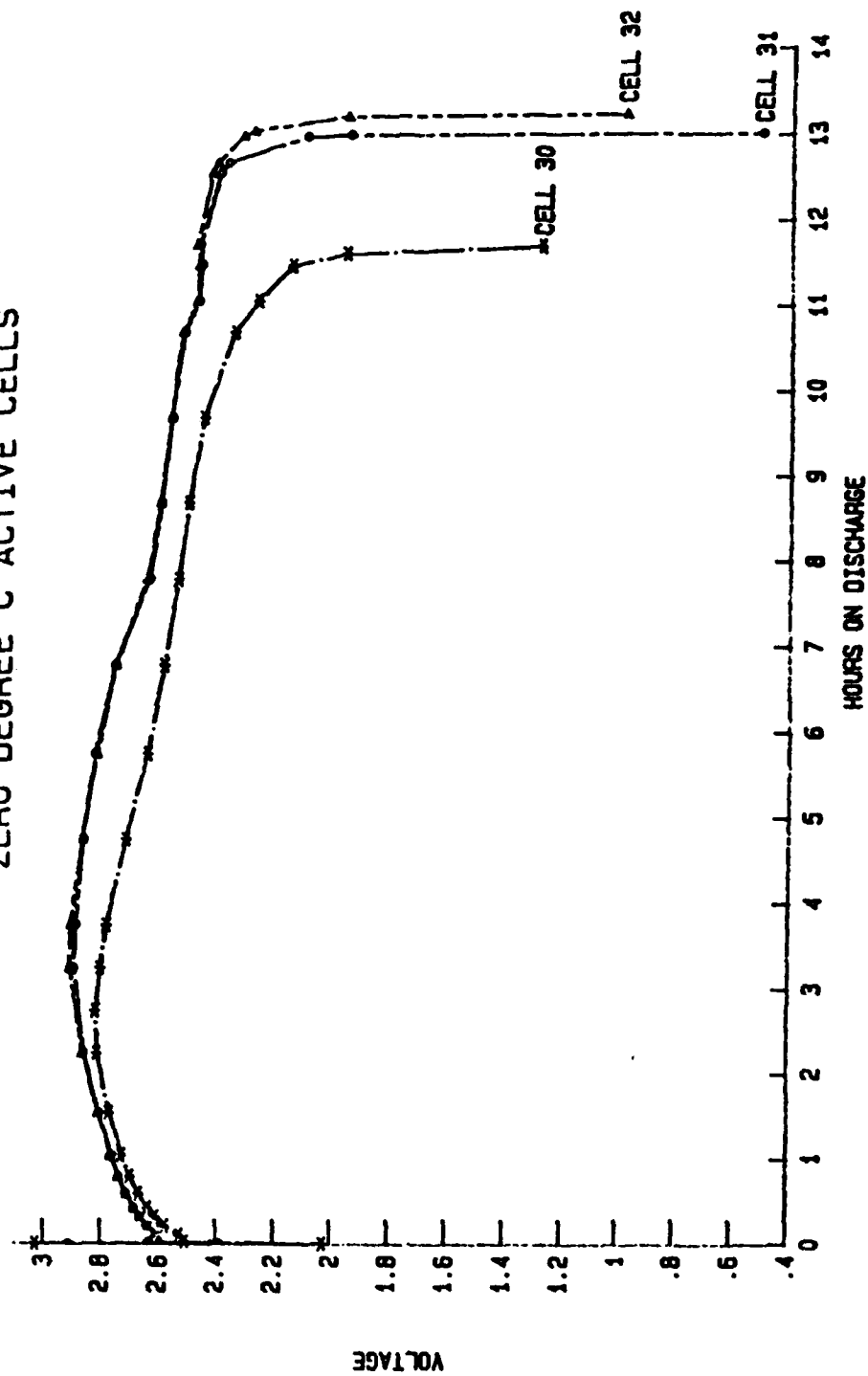
CA/SOCL2 80 MA DISCHARGE

ZERO DEGREE C ACTIVE CELLS



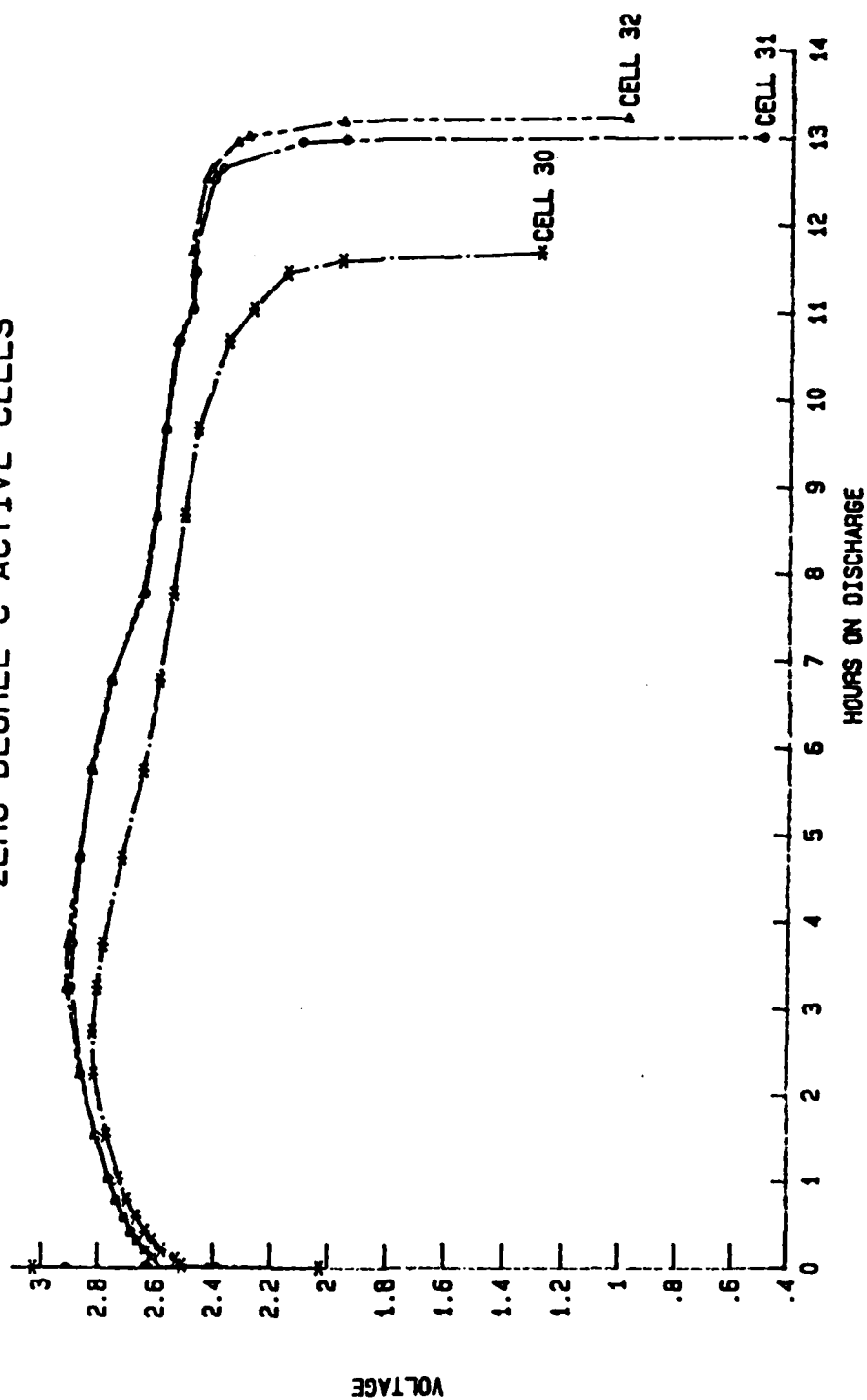
CA/SOCL2 400 MA DISCHARGE

ZERO DEGREE C ACTIVE CELLS



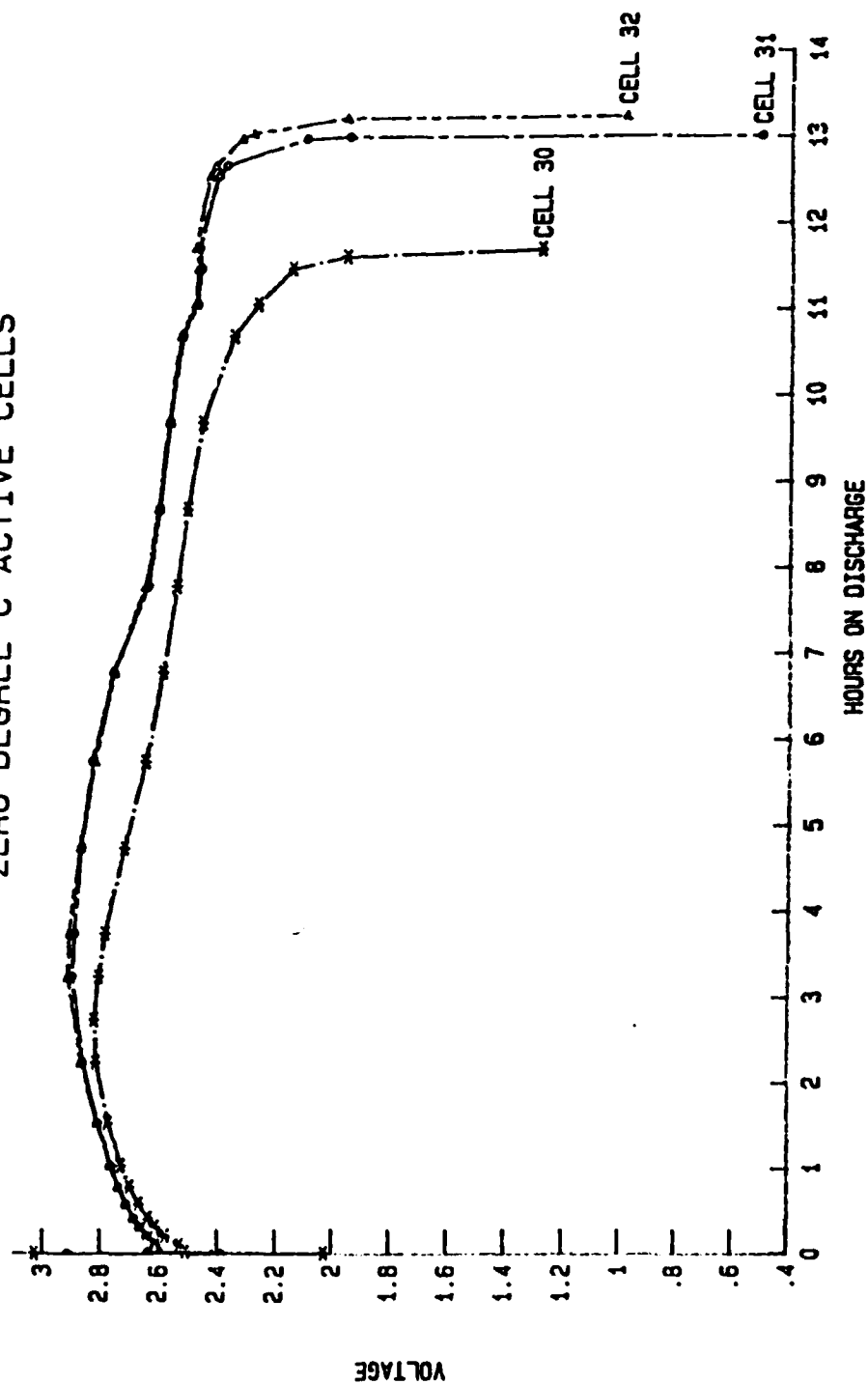
CA/SOCL2 400 MA DISCHARGE

ZERO DEGREE C ACTIVE CELLS



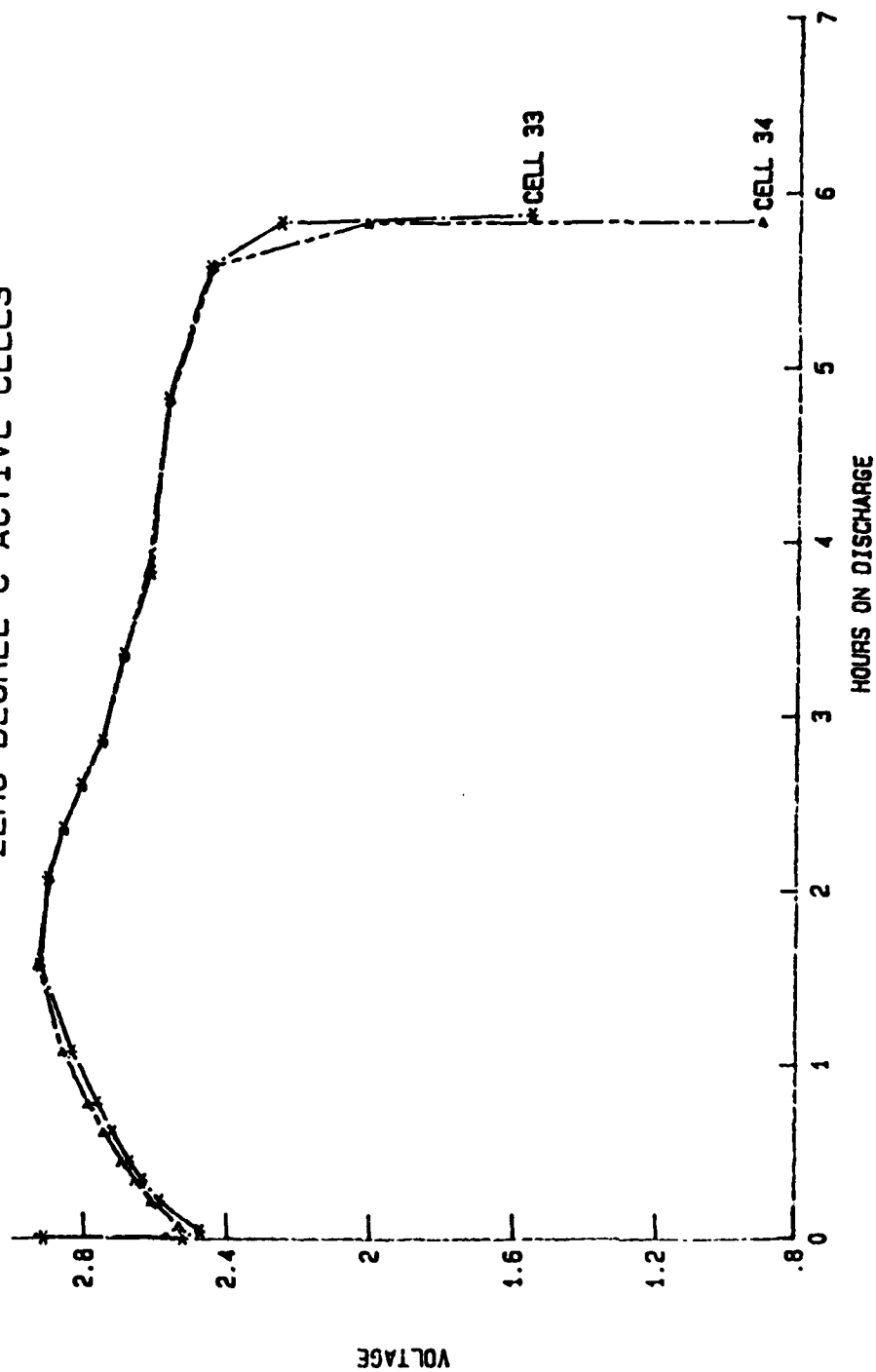
CA/SOCL2 400 MA DISCHARGE

ZERO DEGREE C ACTIVE CELLS



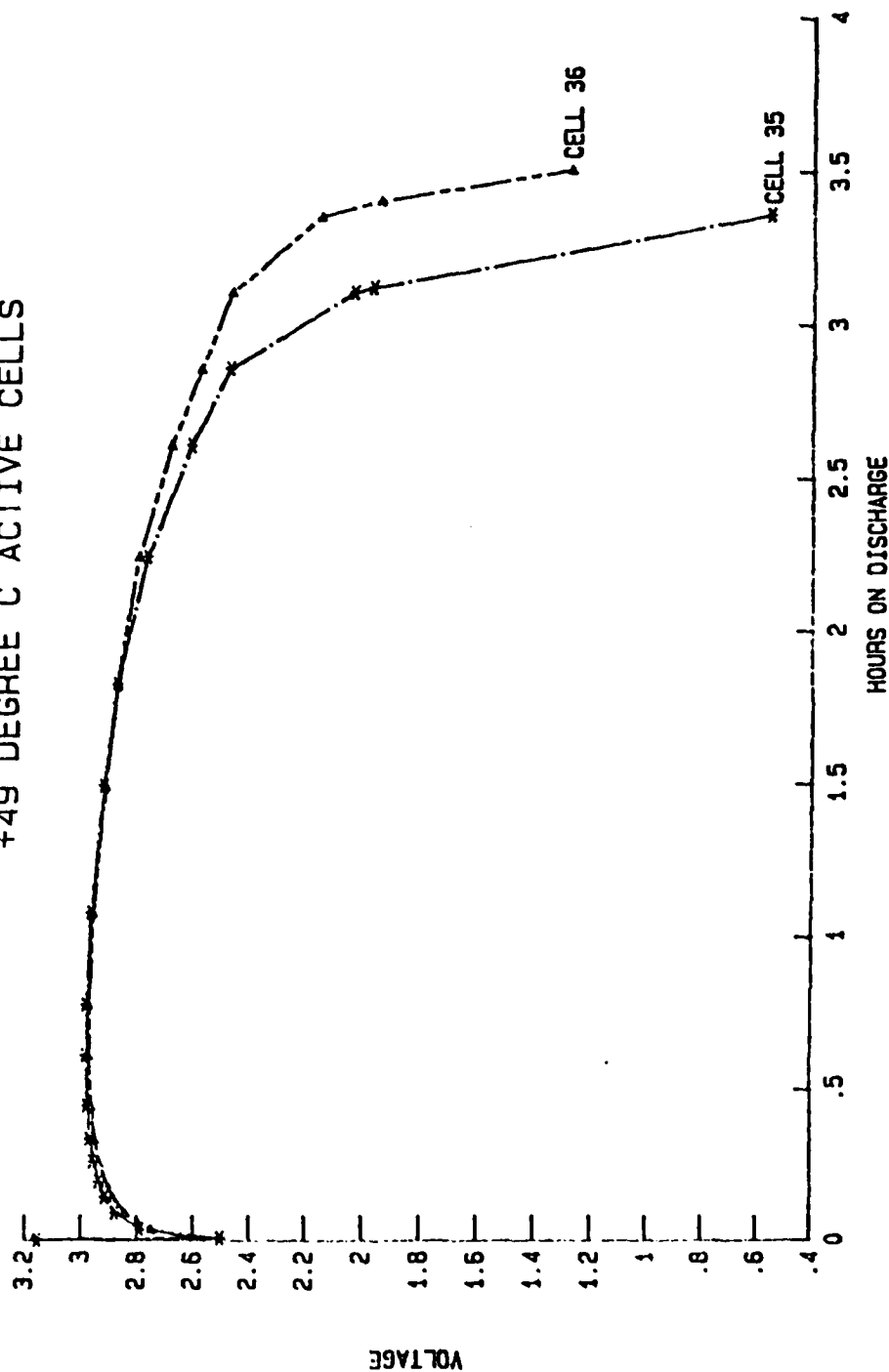
CA/SOCL2 800 MA DISCHARGE

ZERO DEGREE C ACTIVE CELLS



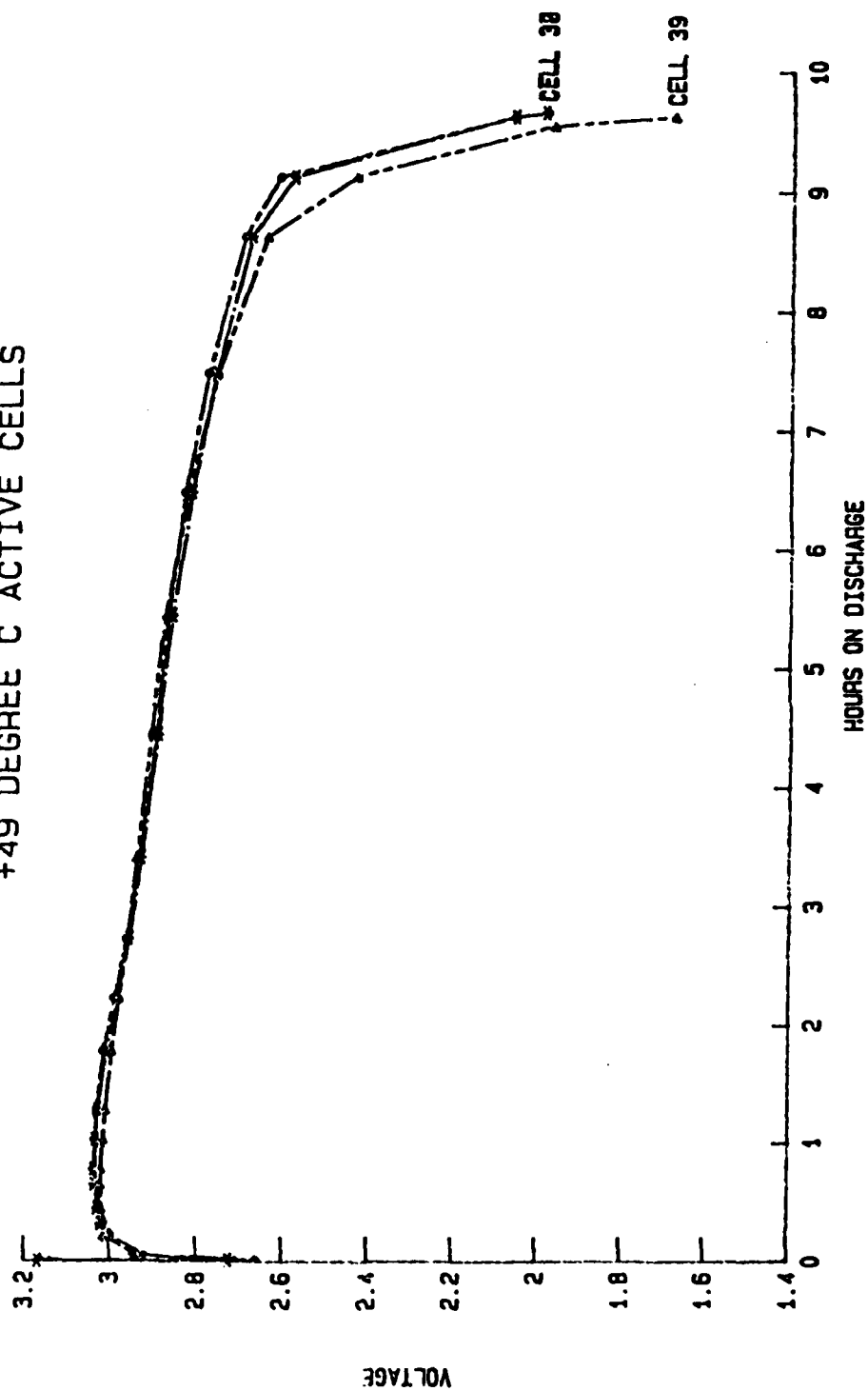
CA/SOCL2 800 MA DISCHARGE

+49 DEGREE C ACTIVE CELLS



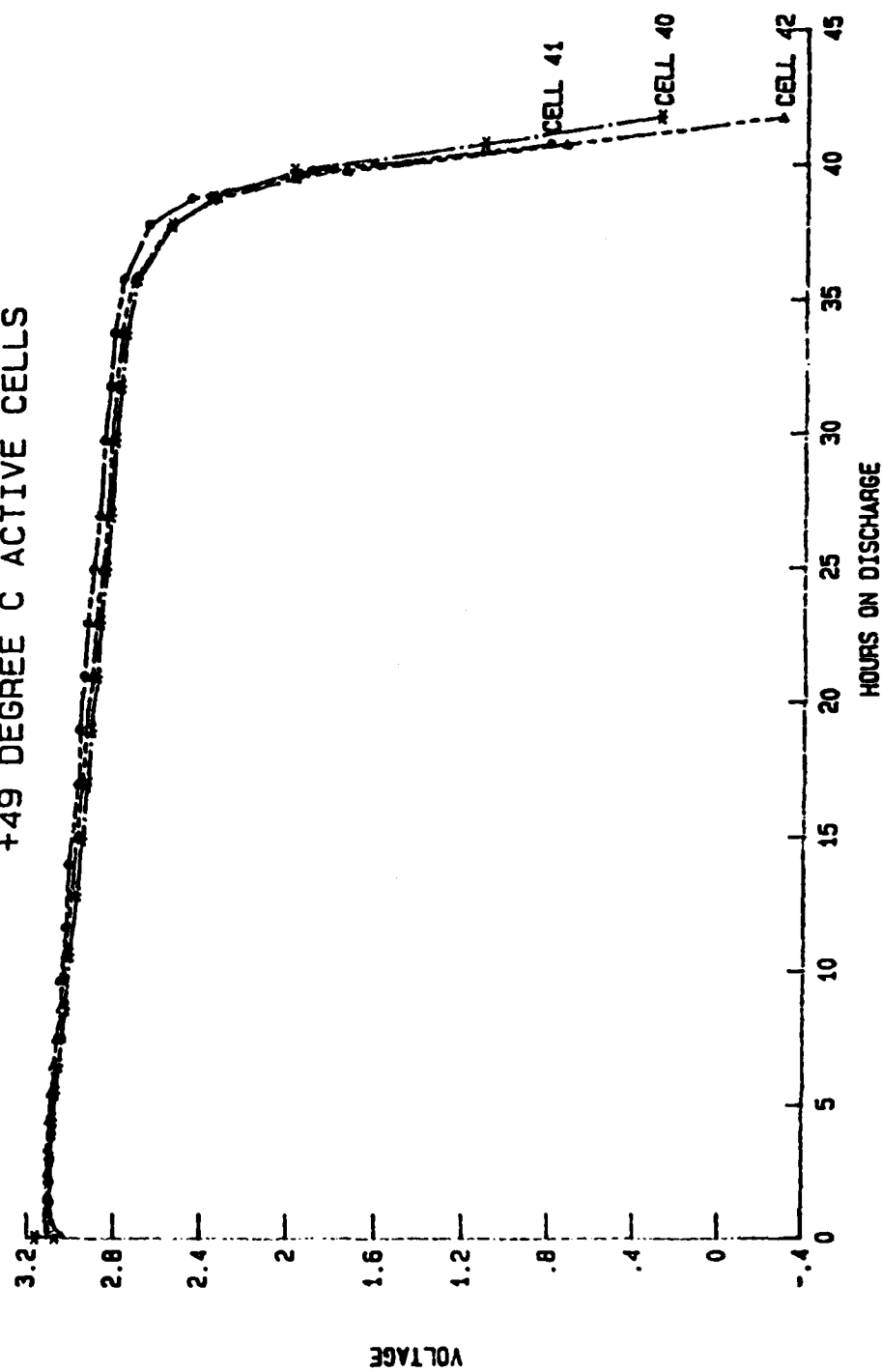
CA/SOCL2 400 MA DISCHARGE

+49 DEGREE C ACTIVE CELLS



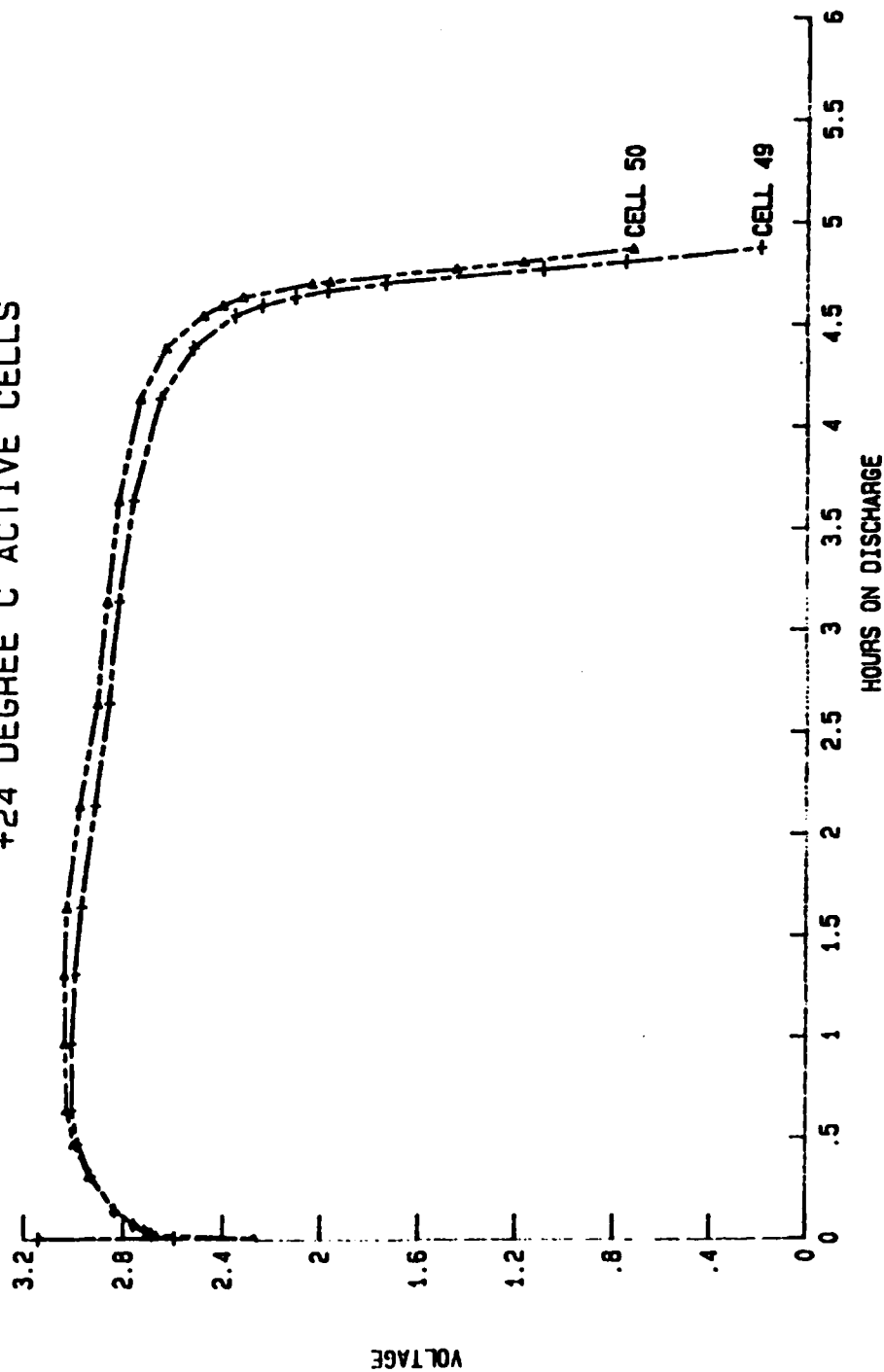
CA/SOCL2 80 MA DISCHARGE

+49 DEGREE C ACTIVE CELLS



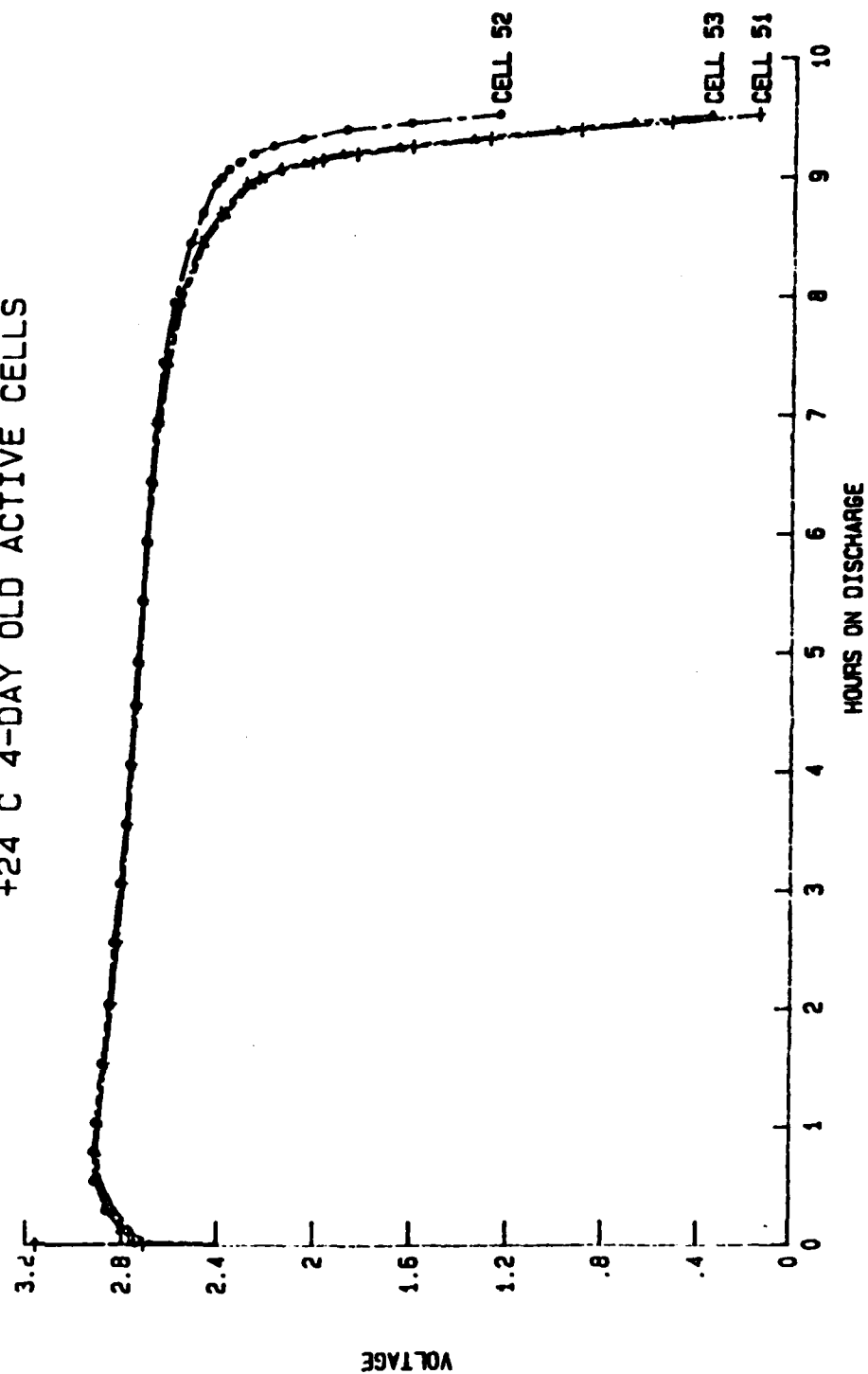
CA/SOCL2 800 MA DISCHARGE

+24 DEGREE C ACTIVE CELLS



CA/SOCL2 400 MA DISCHARGE

+24 C 4-DAY OLD ACTIVE CELLS



APPENDIX D

RESERVE CELL DISCHARGE CURVES

CA/SOCL2 RESERVE CELL

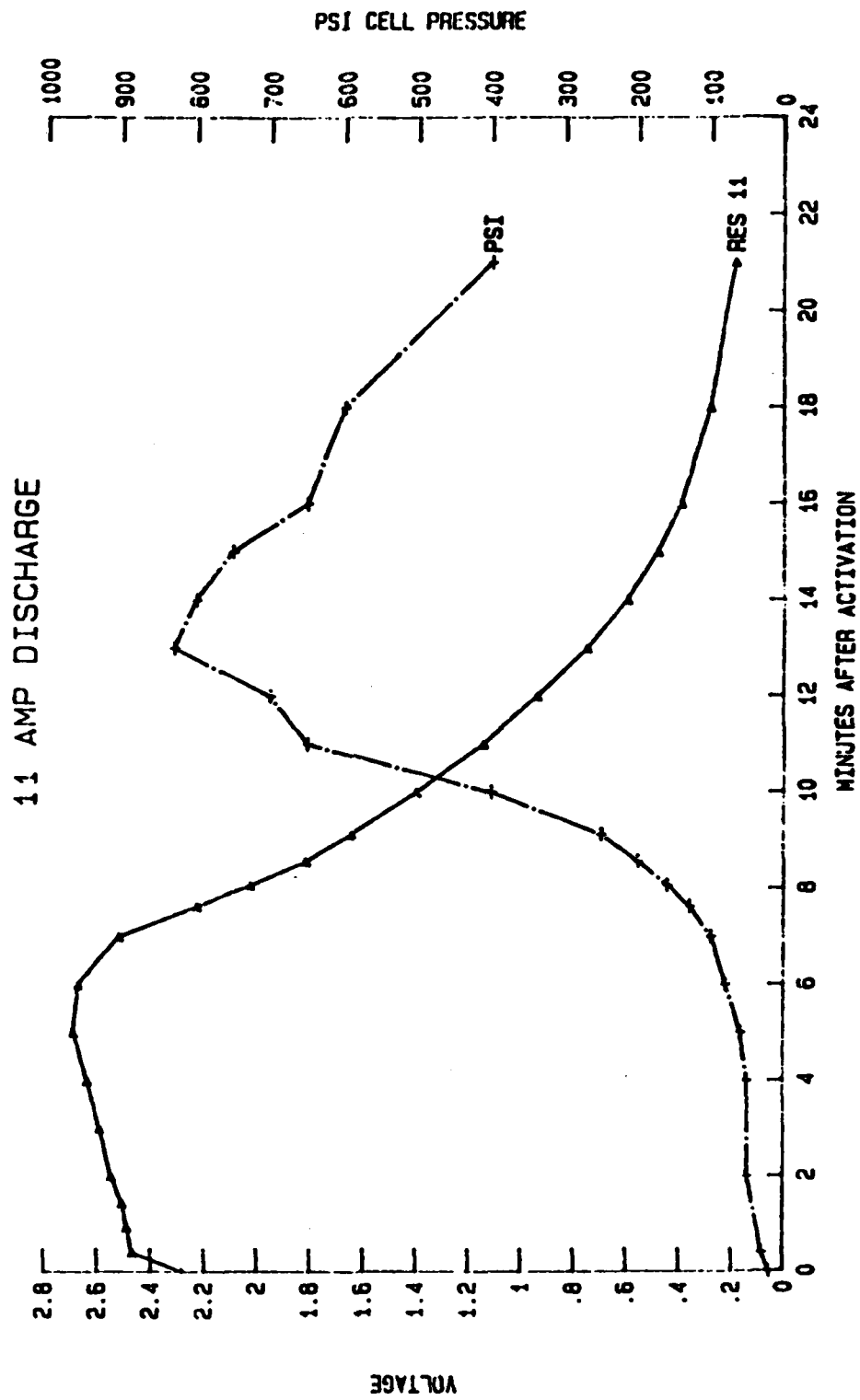


FIGURE D-1 Reserve Cell RES 11 Discharge Curves

TEMP VS TIME

RESERVE CELL 11

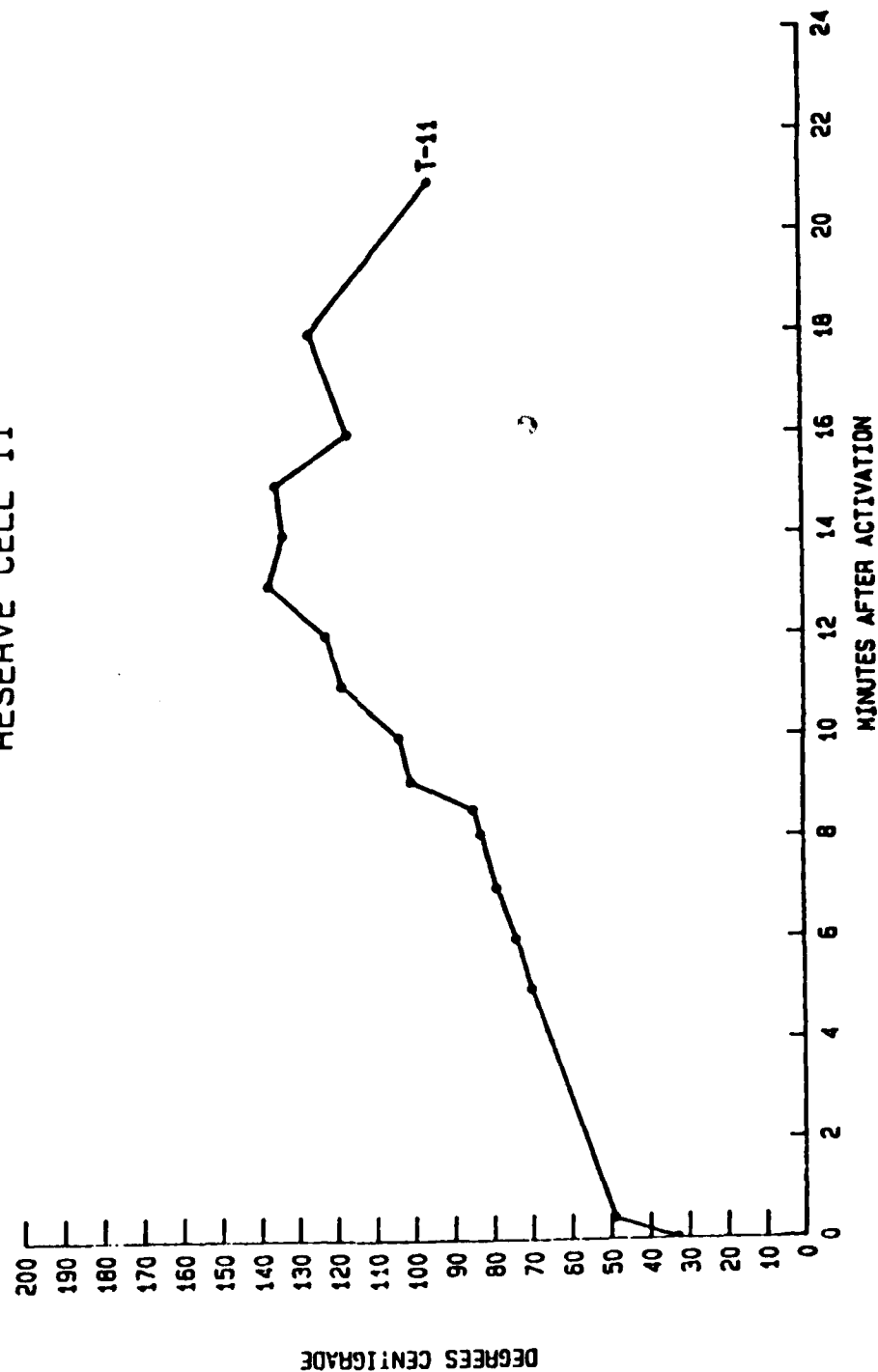


FIGURE D-2 Reserve Cell 11 Discharge Temperature Curve

CA/SOCL2 RESERVE CELL

11 AMP DISCHARGE

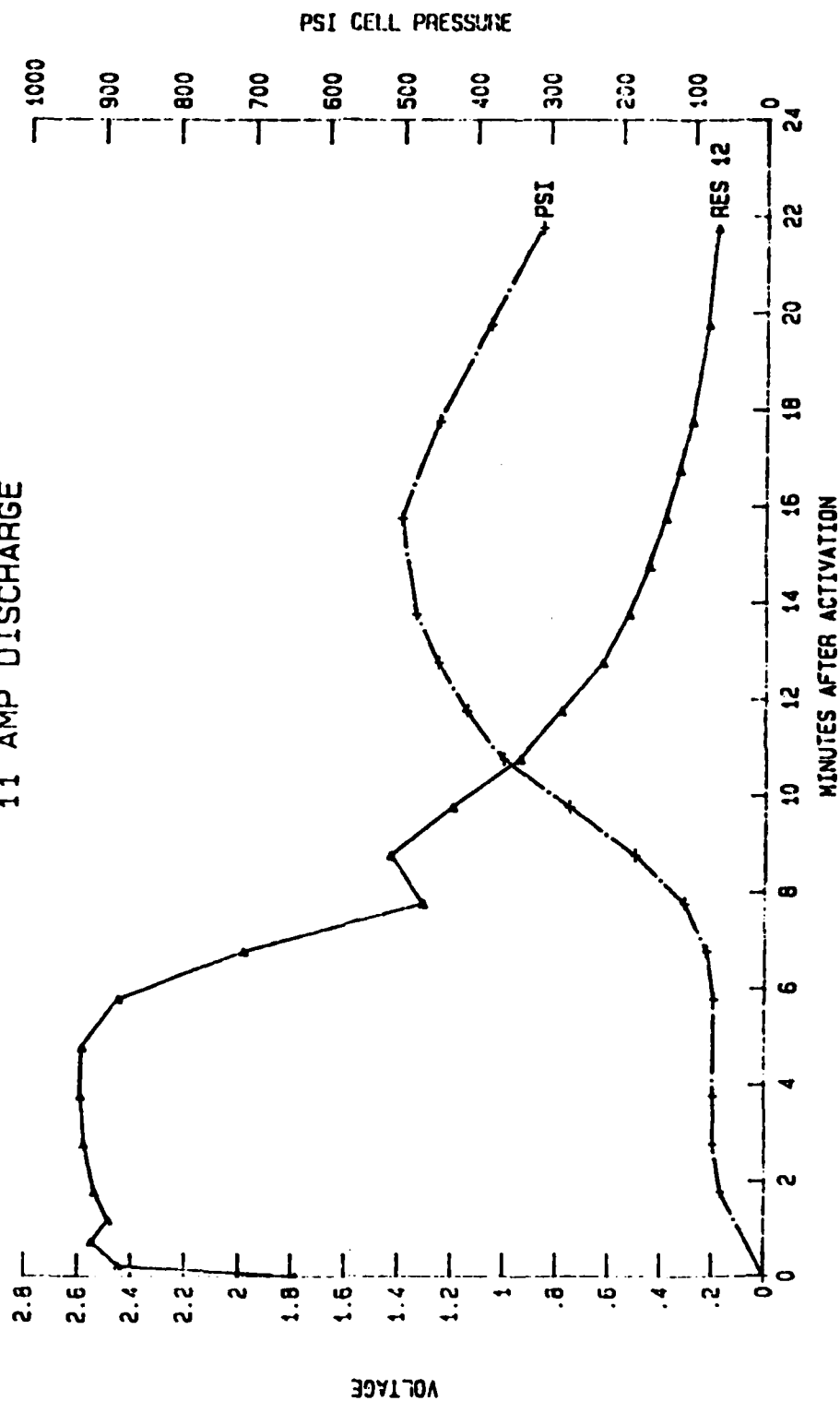


FIGURE D-3 Reserve Cell RES 12 Discharge Curves

TEMP VS TIME

RESERVE CELL 12

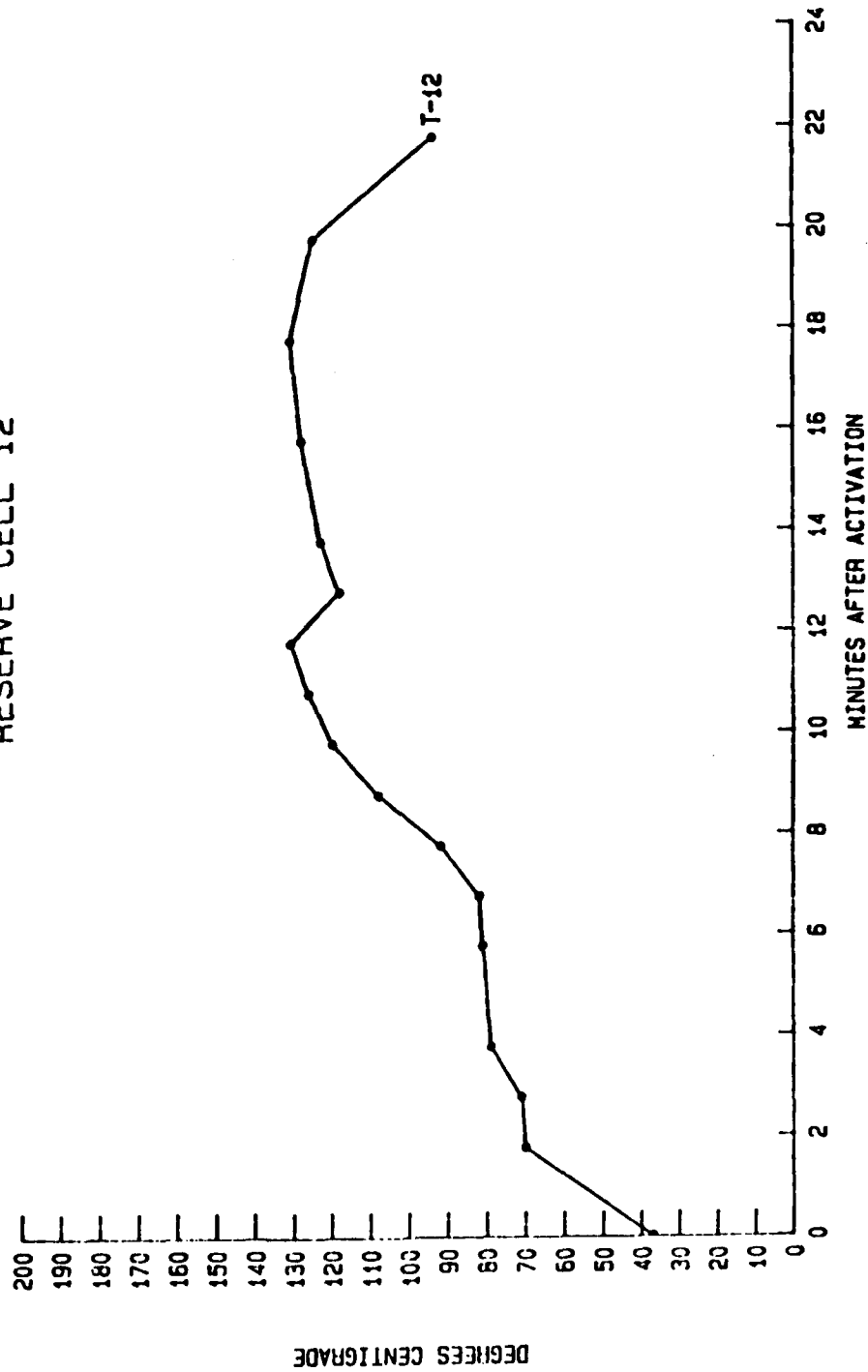


FIGURE D-4 Reserve Cell RES 12 Discharge Temperature Curve

CA/SOCL2 RESERVE CELL

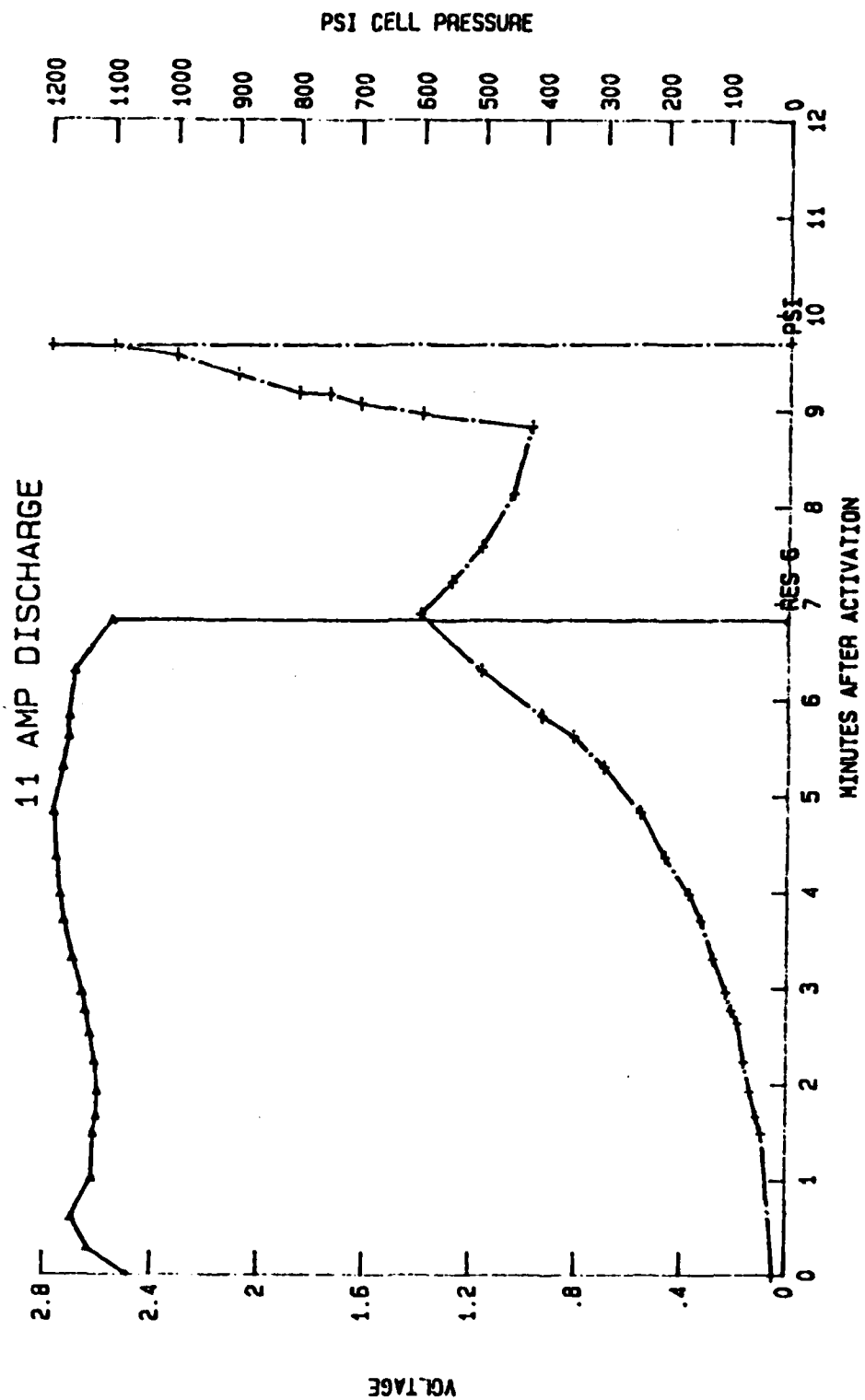


FIGURE D-5 Reserve Cell RES 6 Discharge Curves

TEMP VS TIME

CELL 6 STACK FACE TEMP

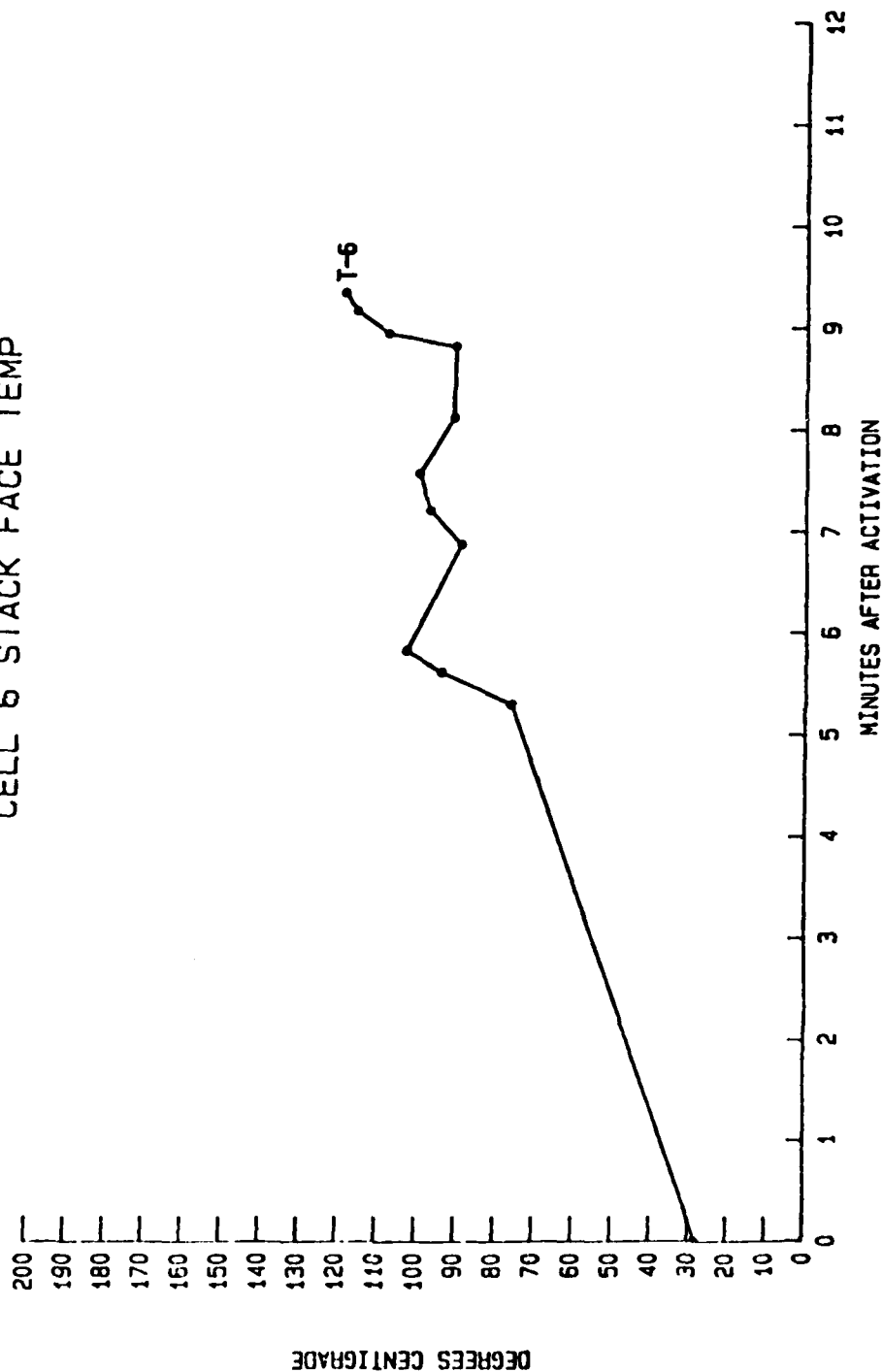


FIGURE D-6 Reserve Cell RES 6 Discharge Temperature Curve

CA/SOCL2 RESERVE CELL

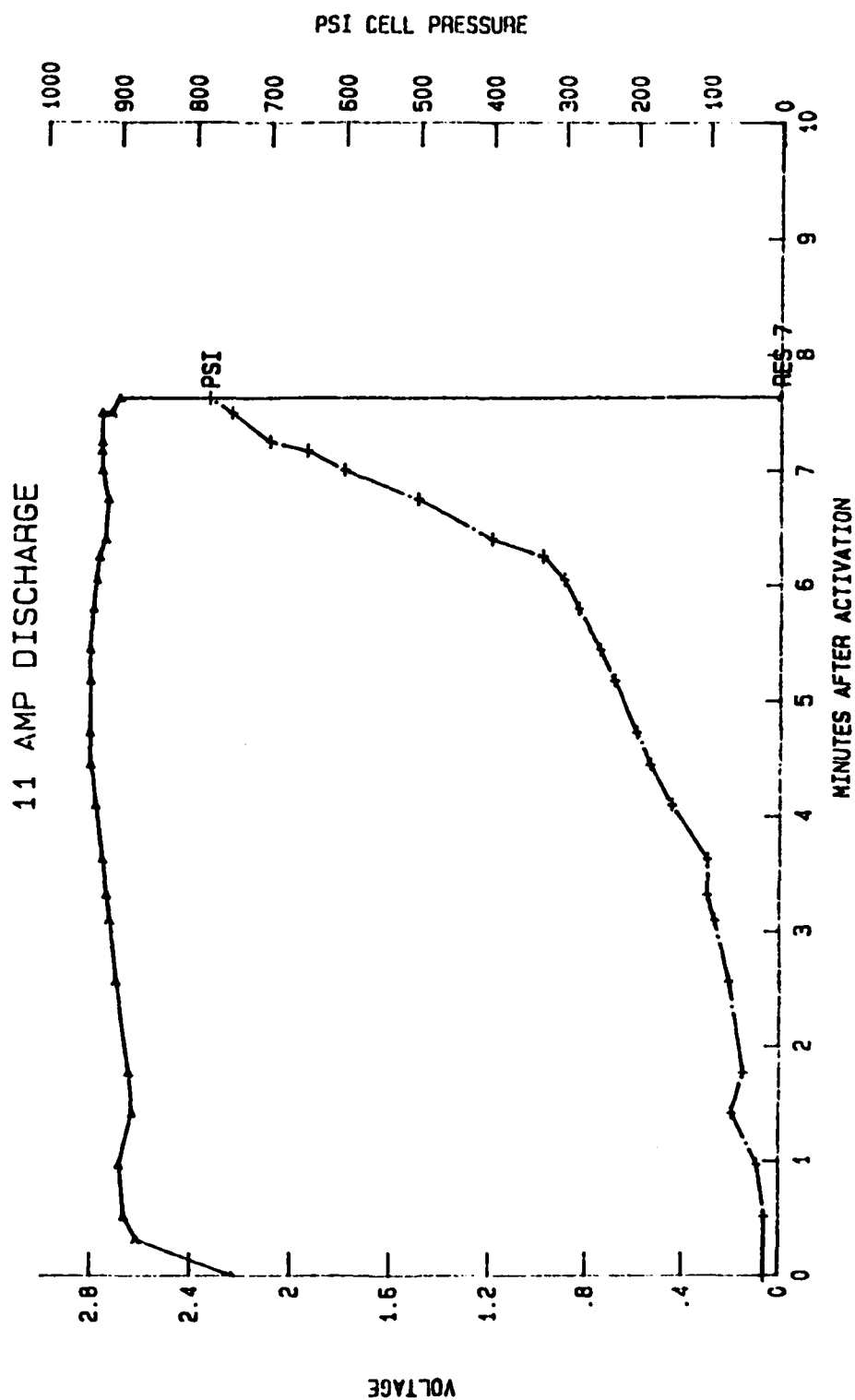


FIGURE D-7 Reserve Cell RES 7 Discharge Curves

TEMP VS TIME

RESERVE CELL 7

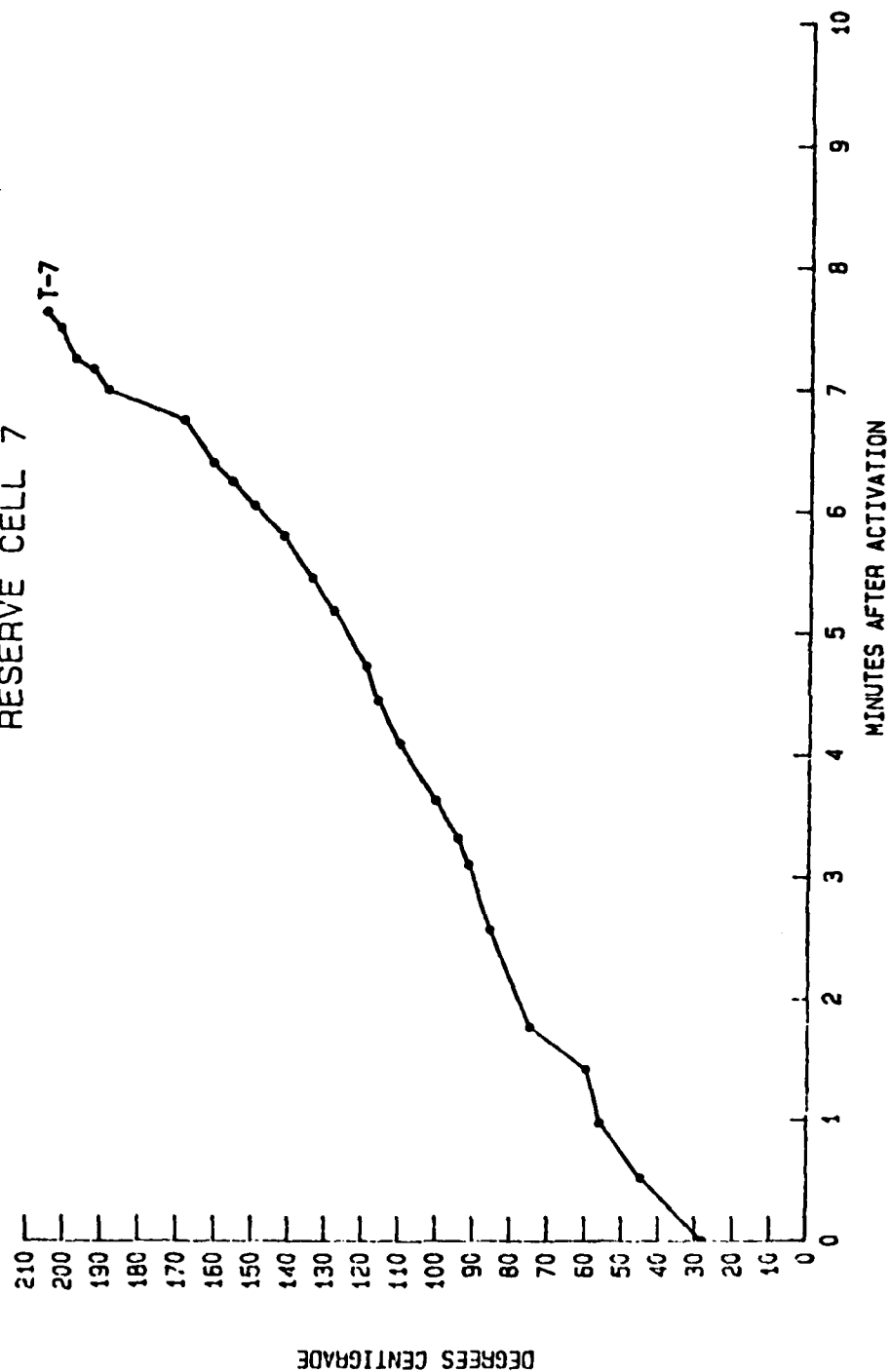


FIGURE D-8 Reserve Cell RES 7 Discharge Temperature Curve

CA/SOCL2 RESERVE CELL

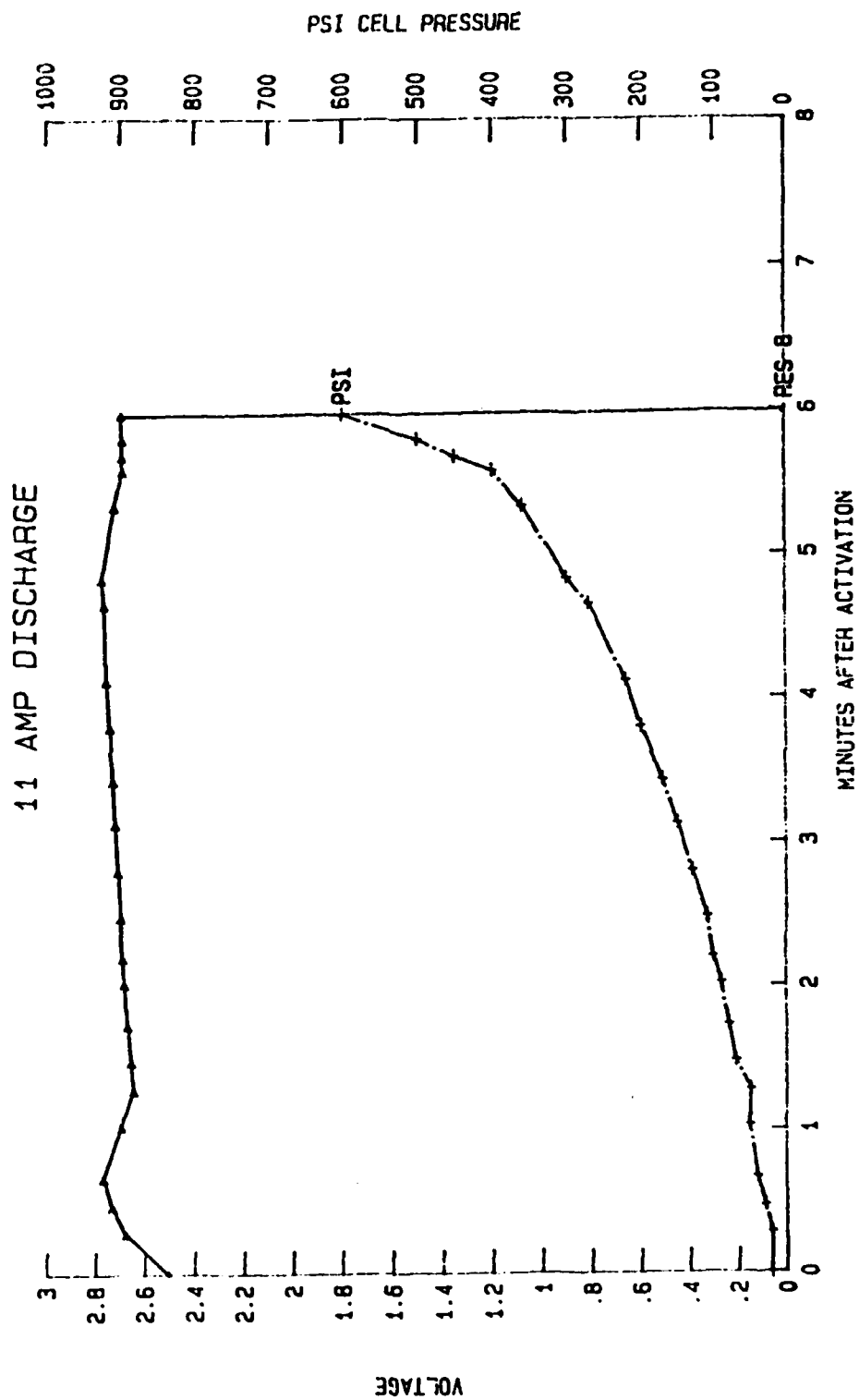


FIGURE D-9 Reserve Cell RES 8 Discharge Curves

TEMP VS TIME

RESERVE CELL 8

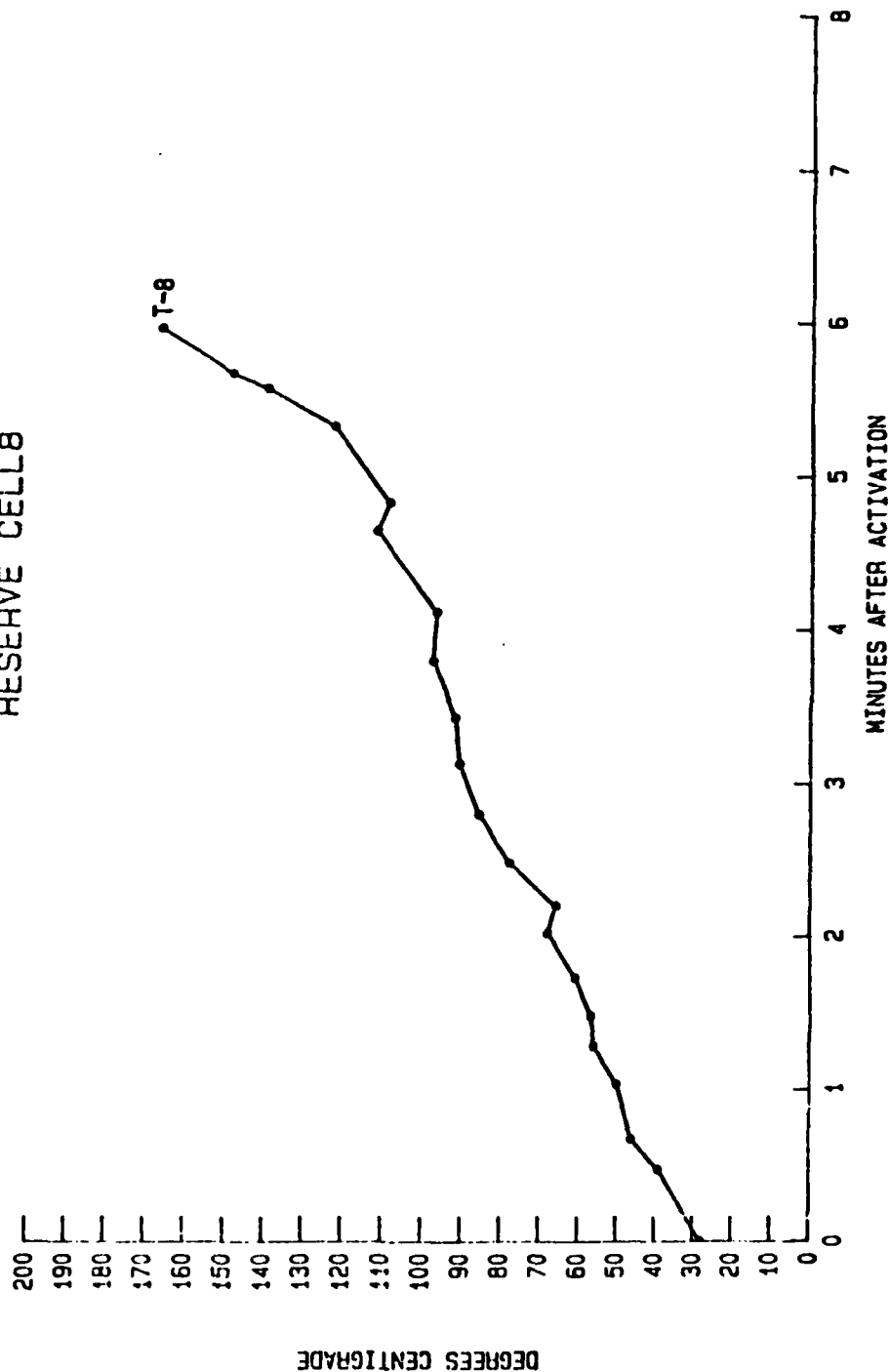


FIGURE D-10 Reserve Cell RES 8 Discharge Temperature Curve

CA/SOCL2 RESERVE CELL

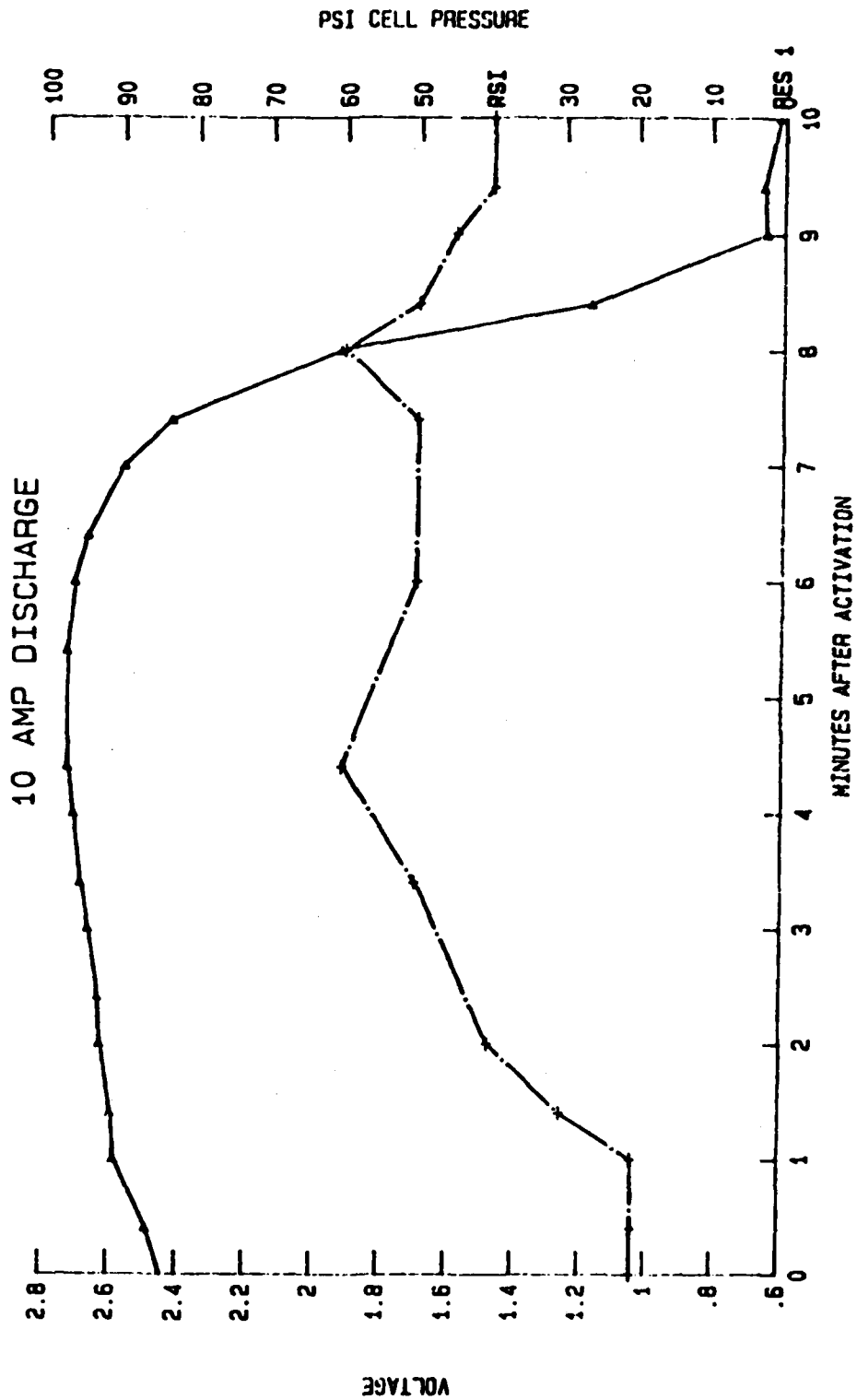
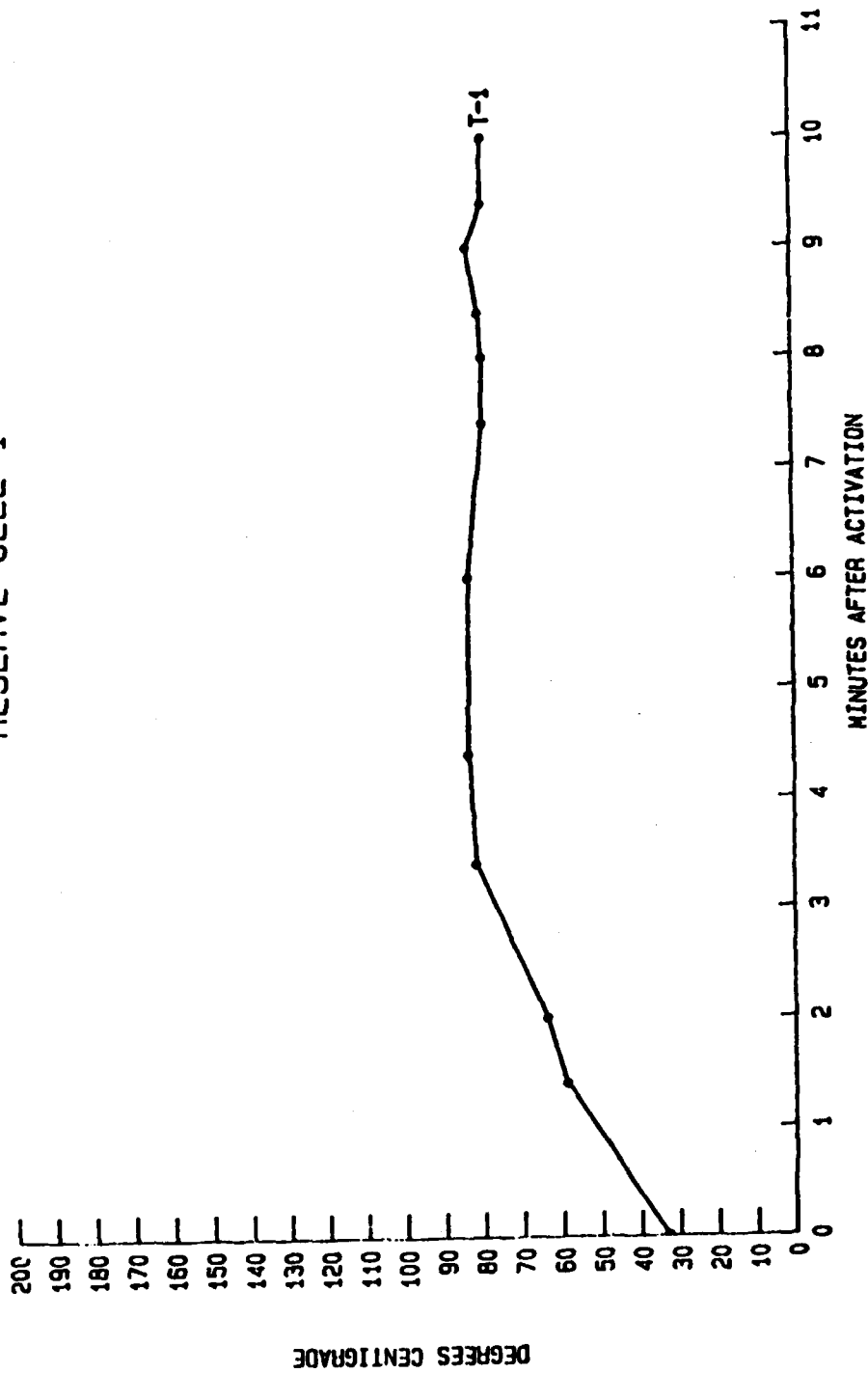


FIGURE D-1 Reserve Cell RES 1 Discharge Curves

TEMP VS TIME

RESERVE CELL 1



FIRUGE D-12 Reserve Cell RES 1 Discharge Temperature Curve

CA/SOCL2 RESERVE CELL

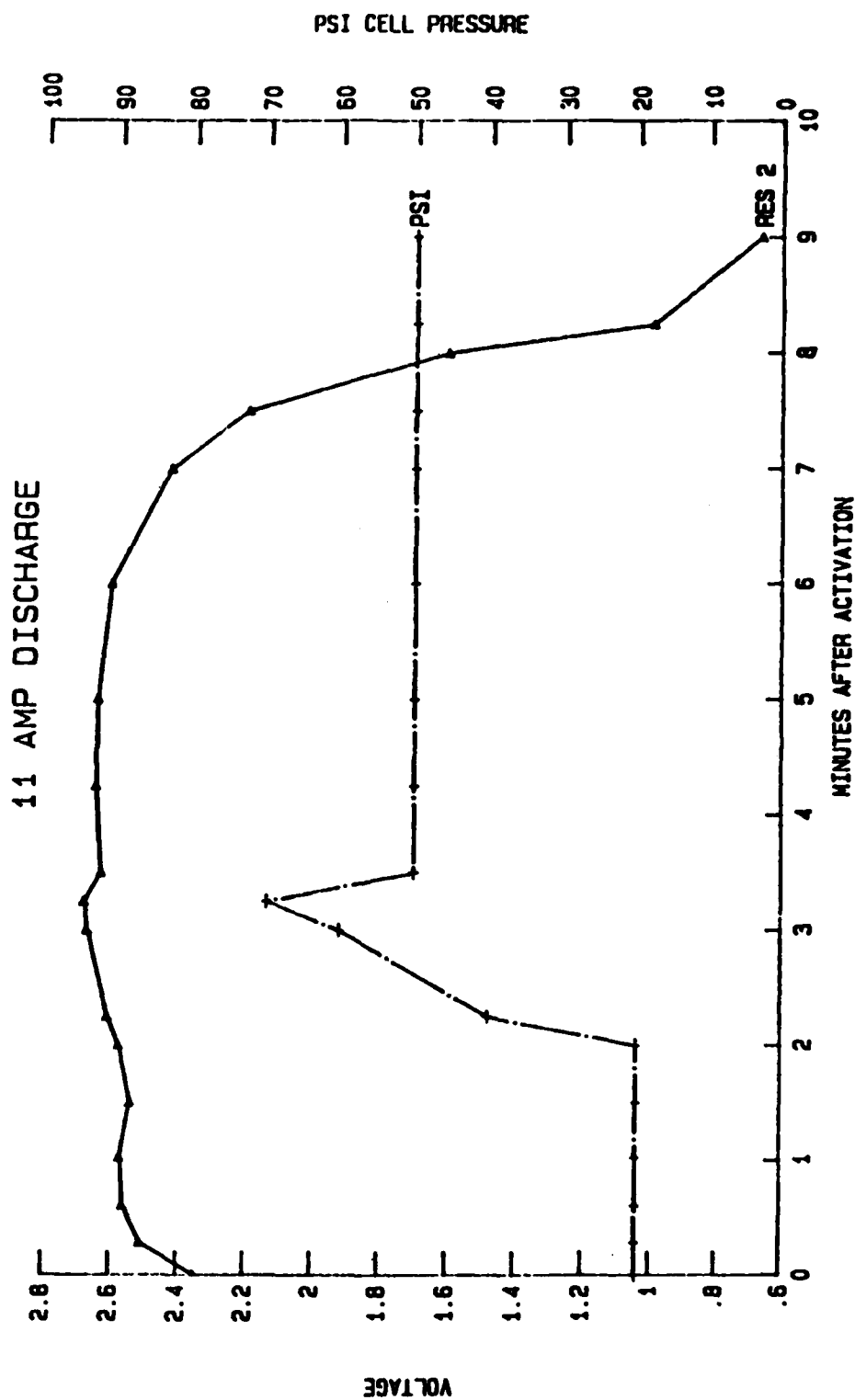


FIGURE D-13 Reserve Cell RES 2 Discharge Curves

TEMP VS TIME

RESERVE CELL 2

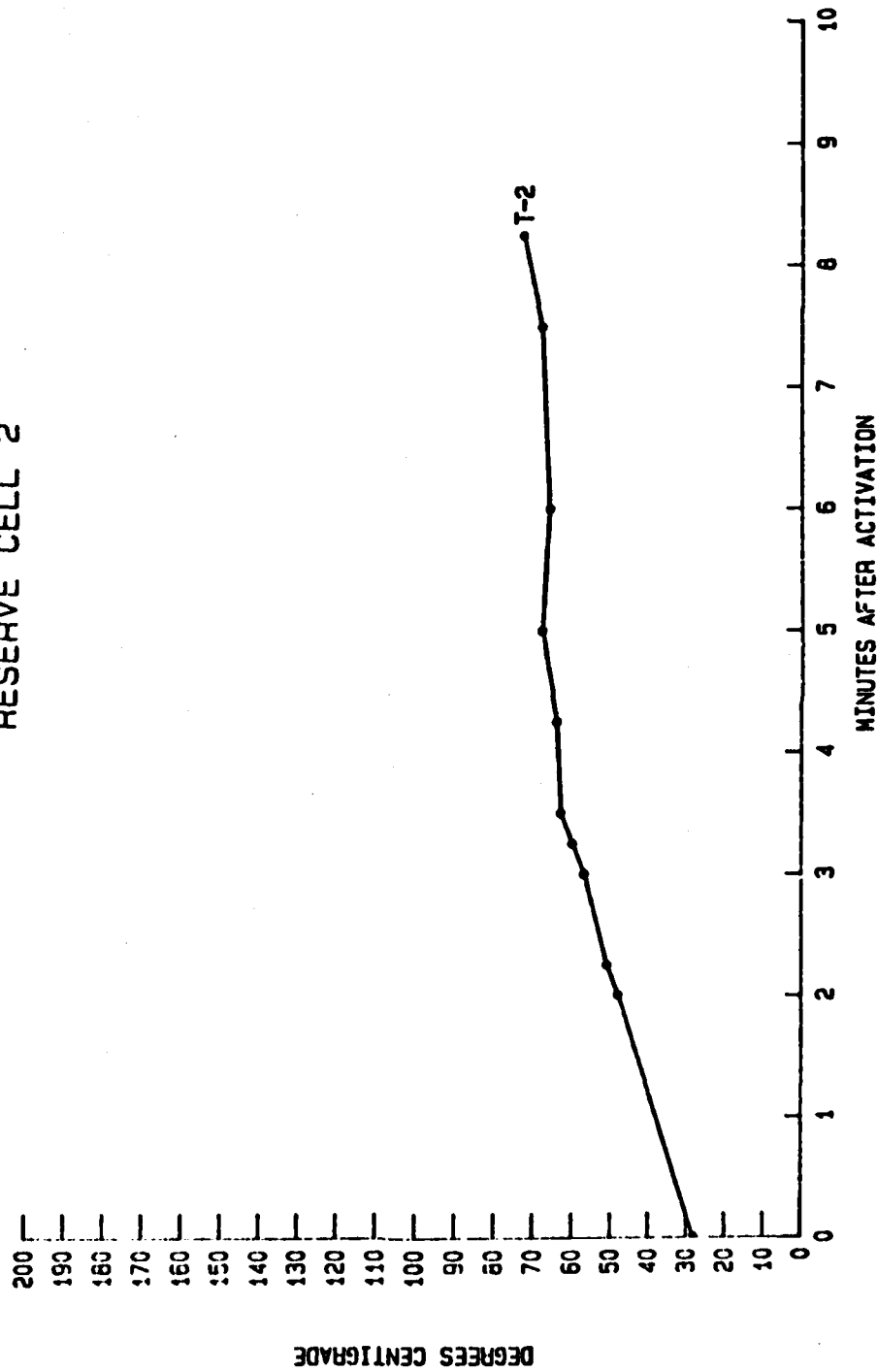


FIGURE D-14 Reserve Cell RES 2 Discharge Temperature Curve

CA/SOCL2 RESERVE CELL

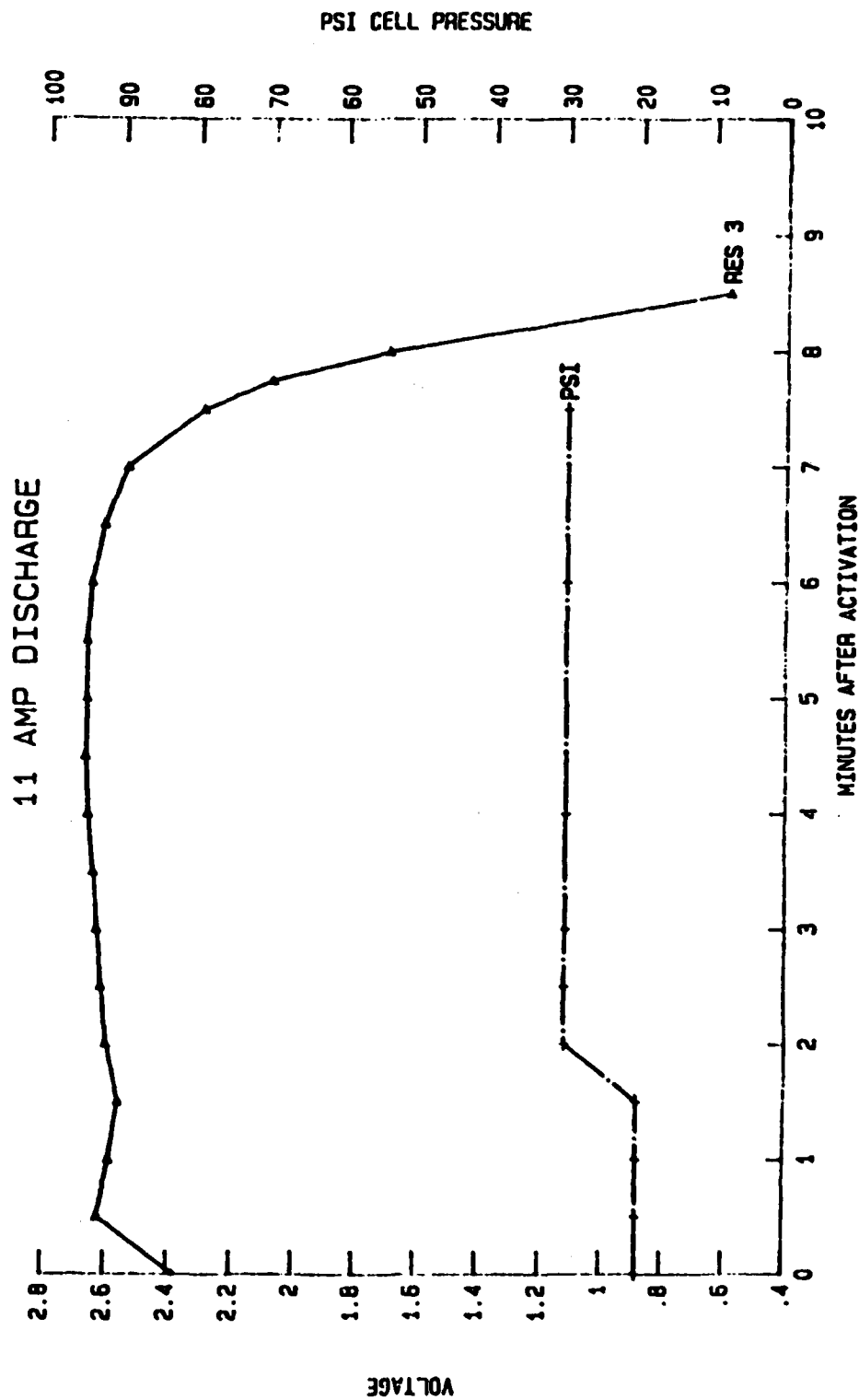


FIGURE D-15 Reserve Cell RES 3 Discharge Curve

TEMP VS TIME

RESERVE CELL 3

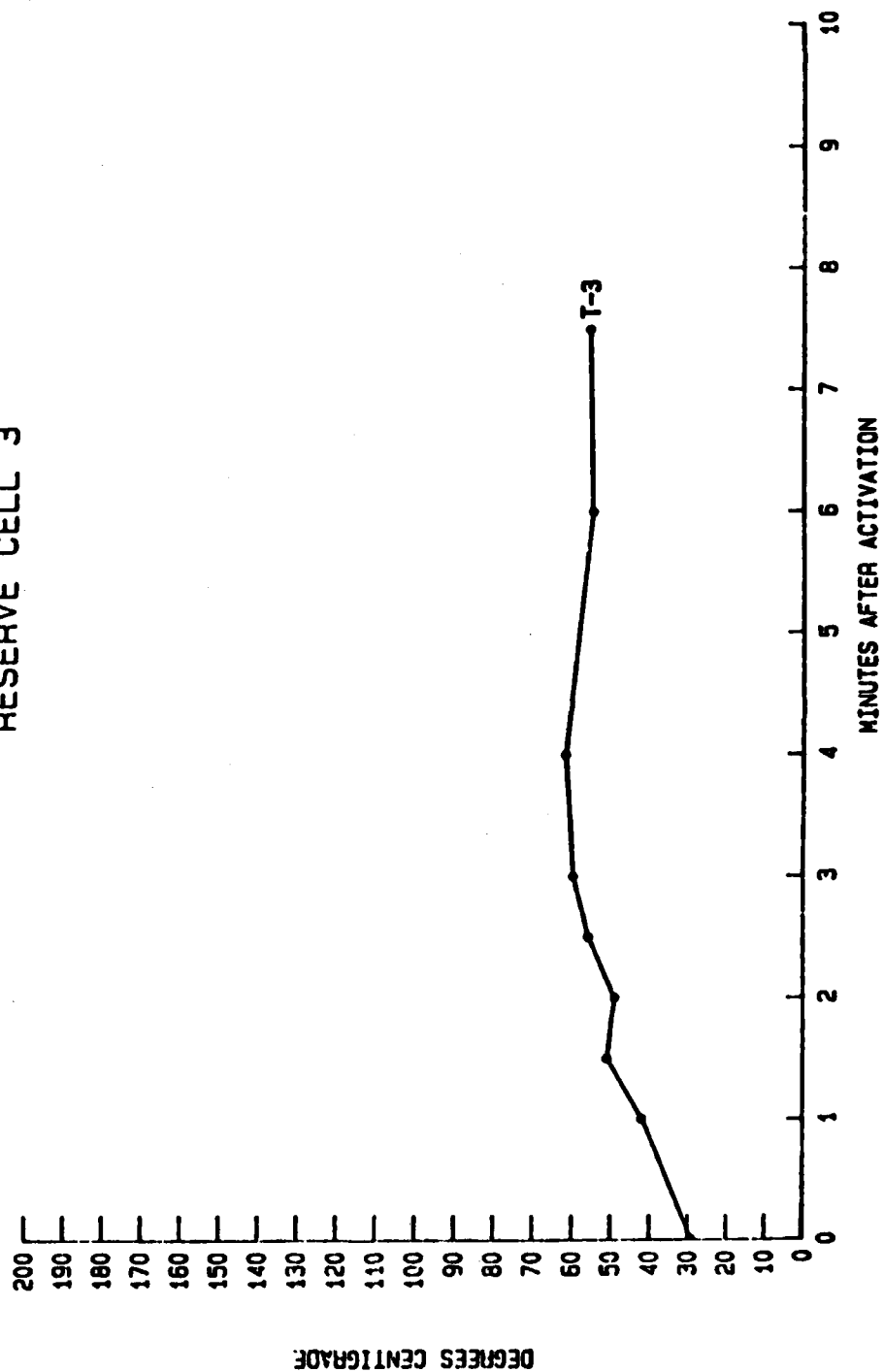


FIGURE D-16 Reserve Cell RES 3 Discharge Temperature Curve

CA/SOCL2 RESERVE CELL

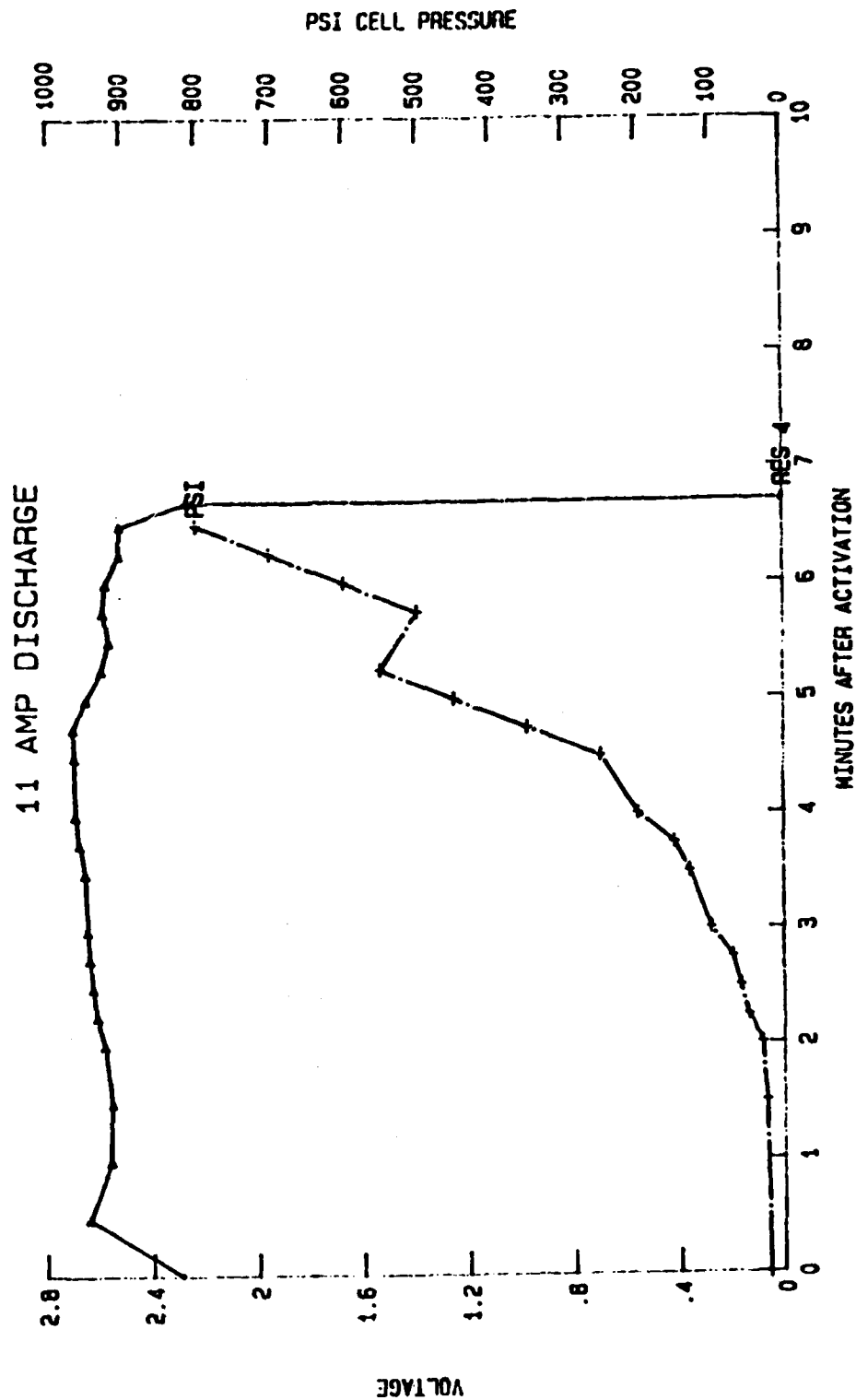


FIGURE D-17 Reserve Cell RES 7 Discharge Curves

CA/SOCL2 RESERVE CELL

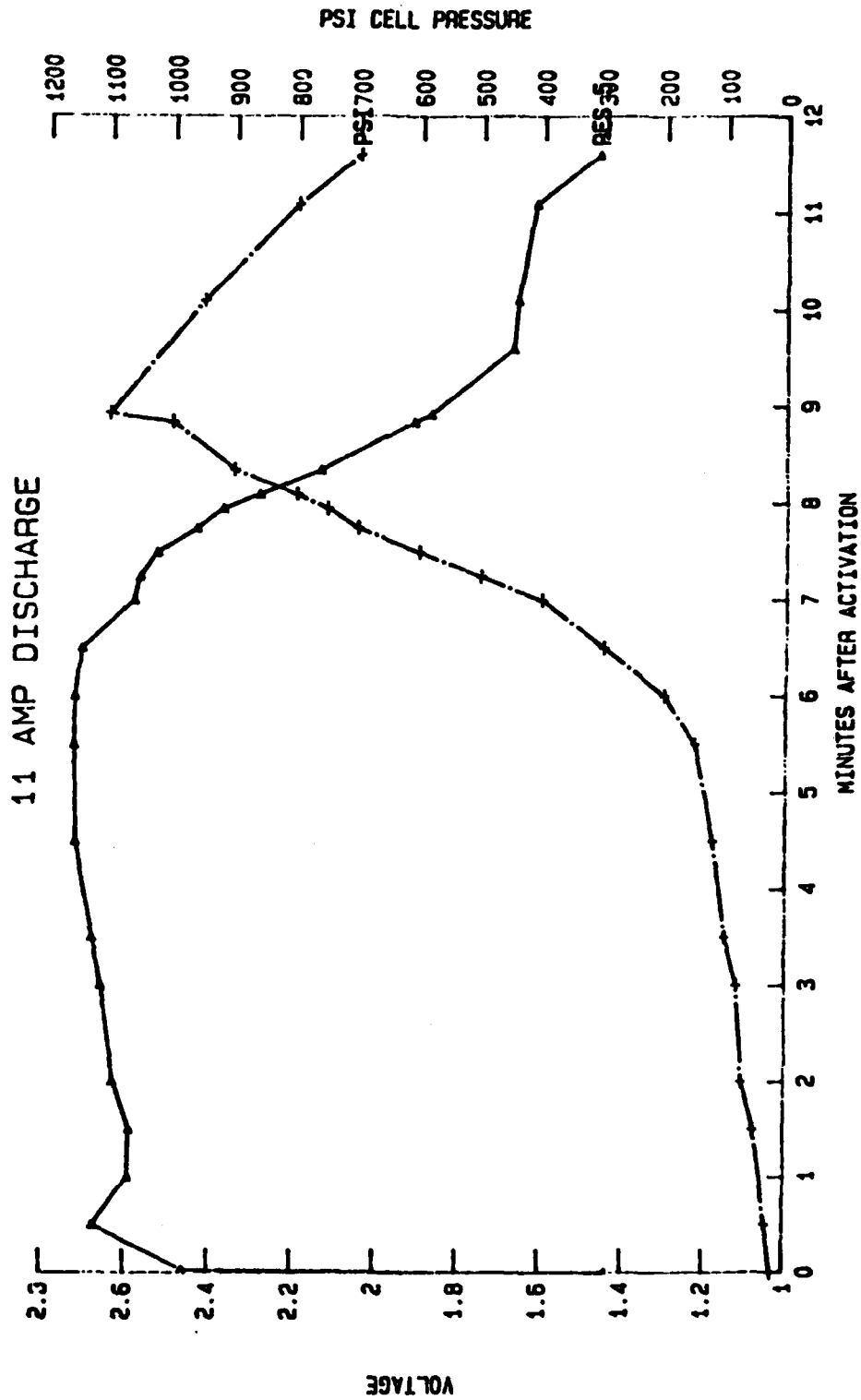


FIGURE D-18 Reserve Cell RES 5 Discharge Curves

TEMP VS TIME

RESERVE CELL 5

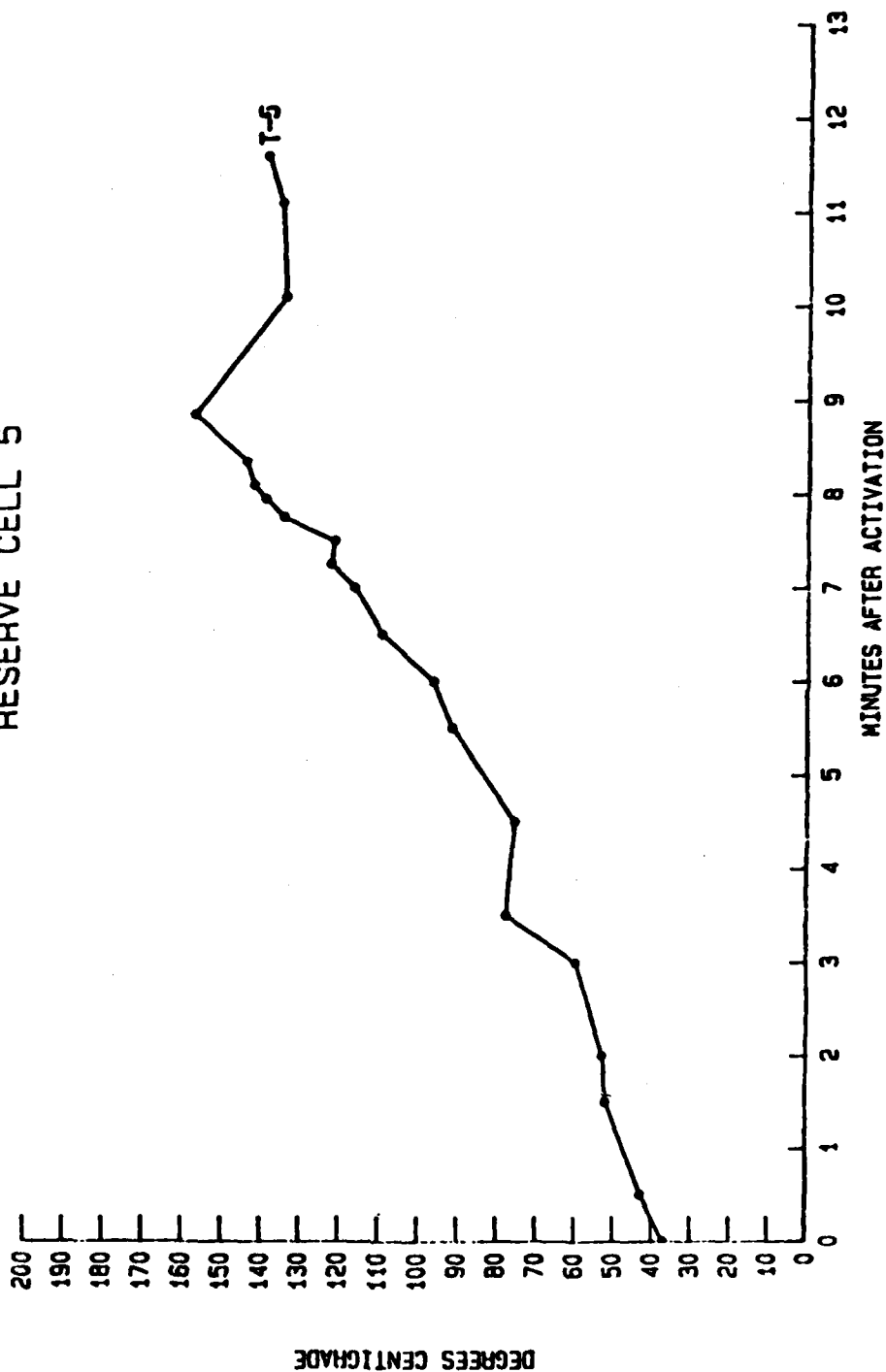


FIGURE D-19 Reserve Cell RES 5 Discharge Temperature Curve

CA/SOCL2 RESERVE CELL

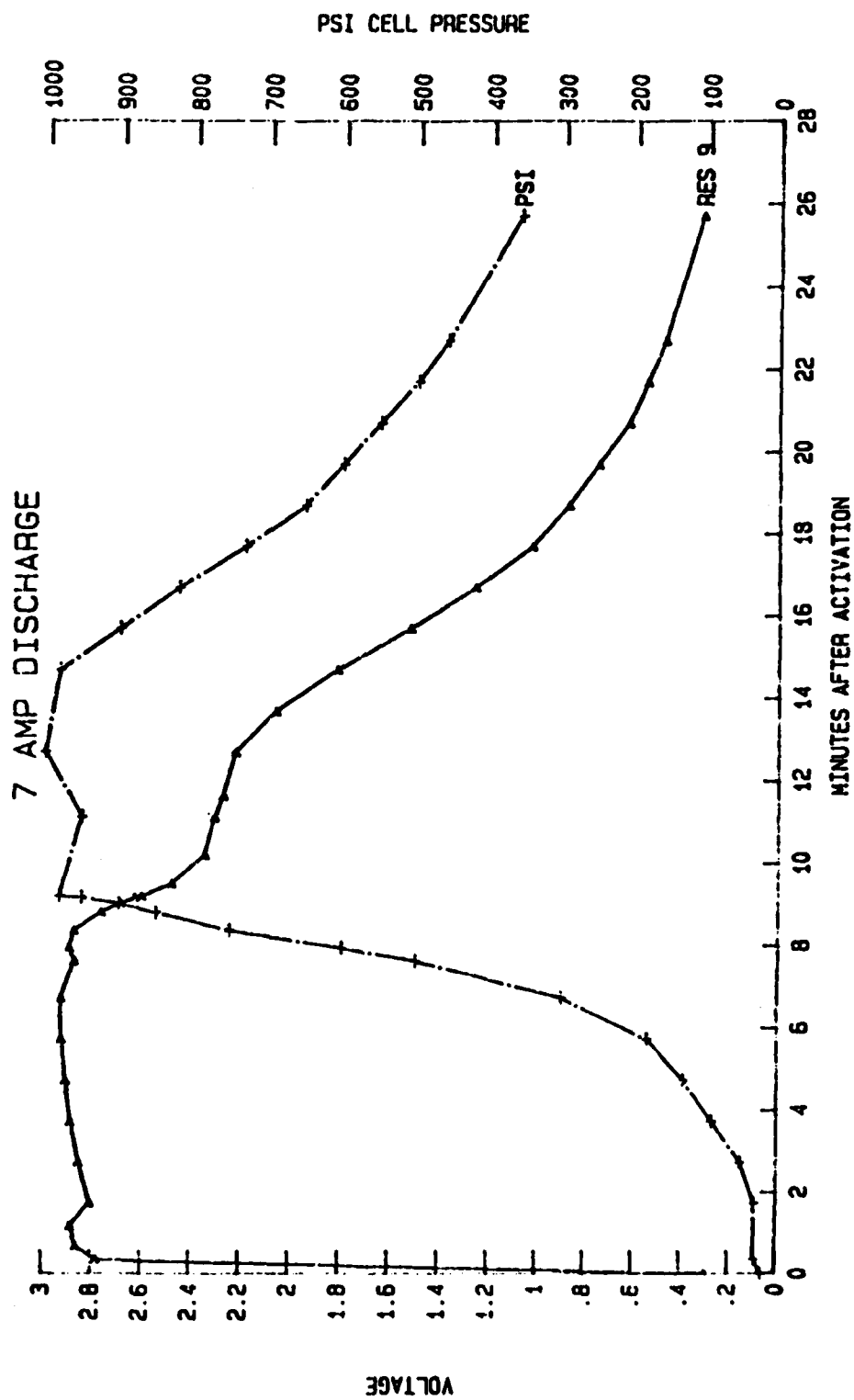


FIGURE D-20 Reserve Cell RES 9 Discharge Curves

TEMP VS TIME

RESERVE CELL 9

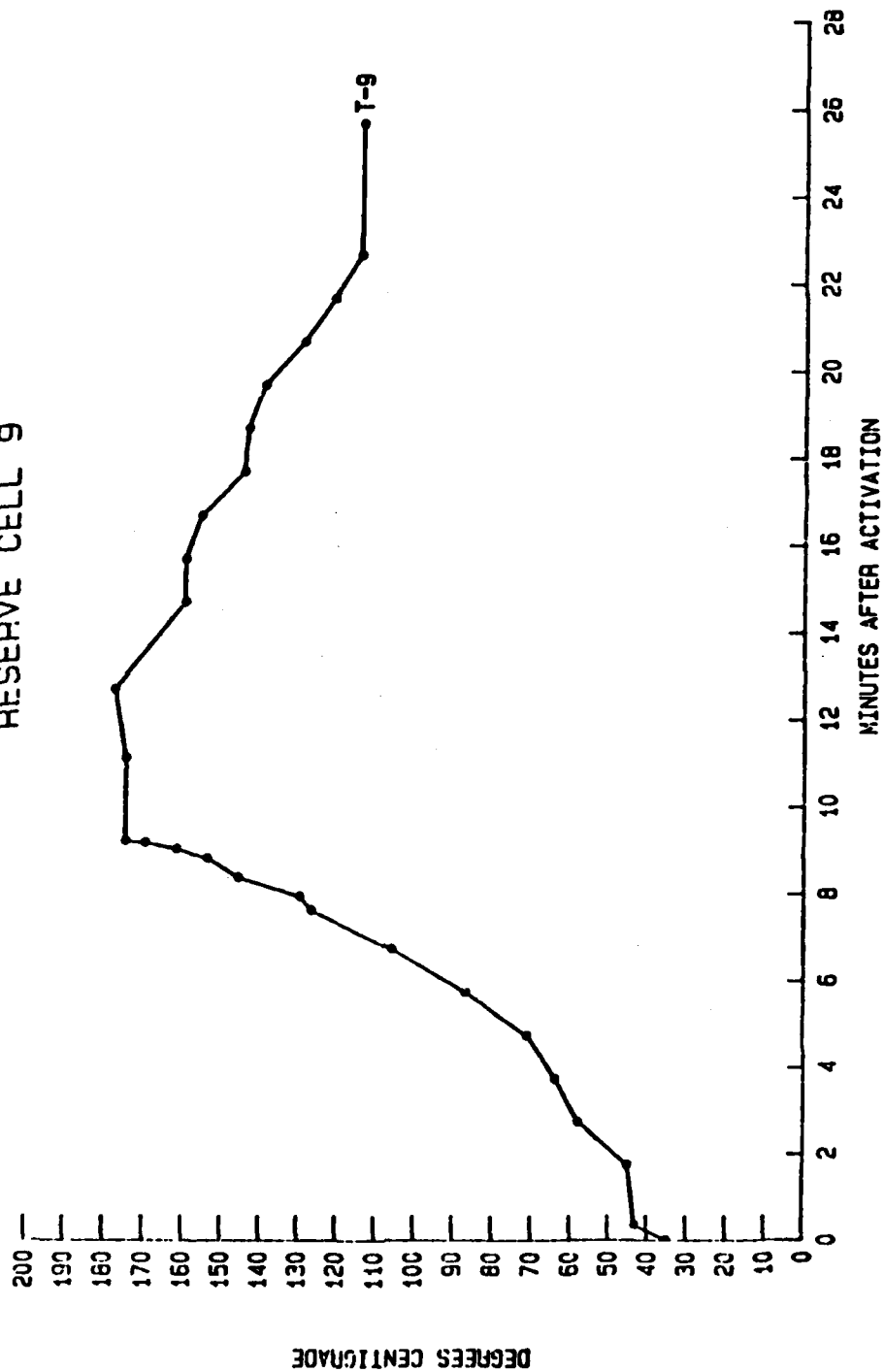


FIGURE D-21 Reserve Cell RES 9 Discharge Temperature Curve

CA/SOCL2 RESERVE CELL

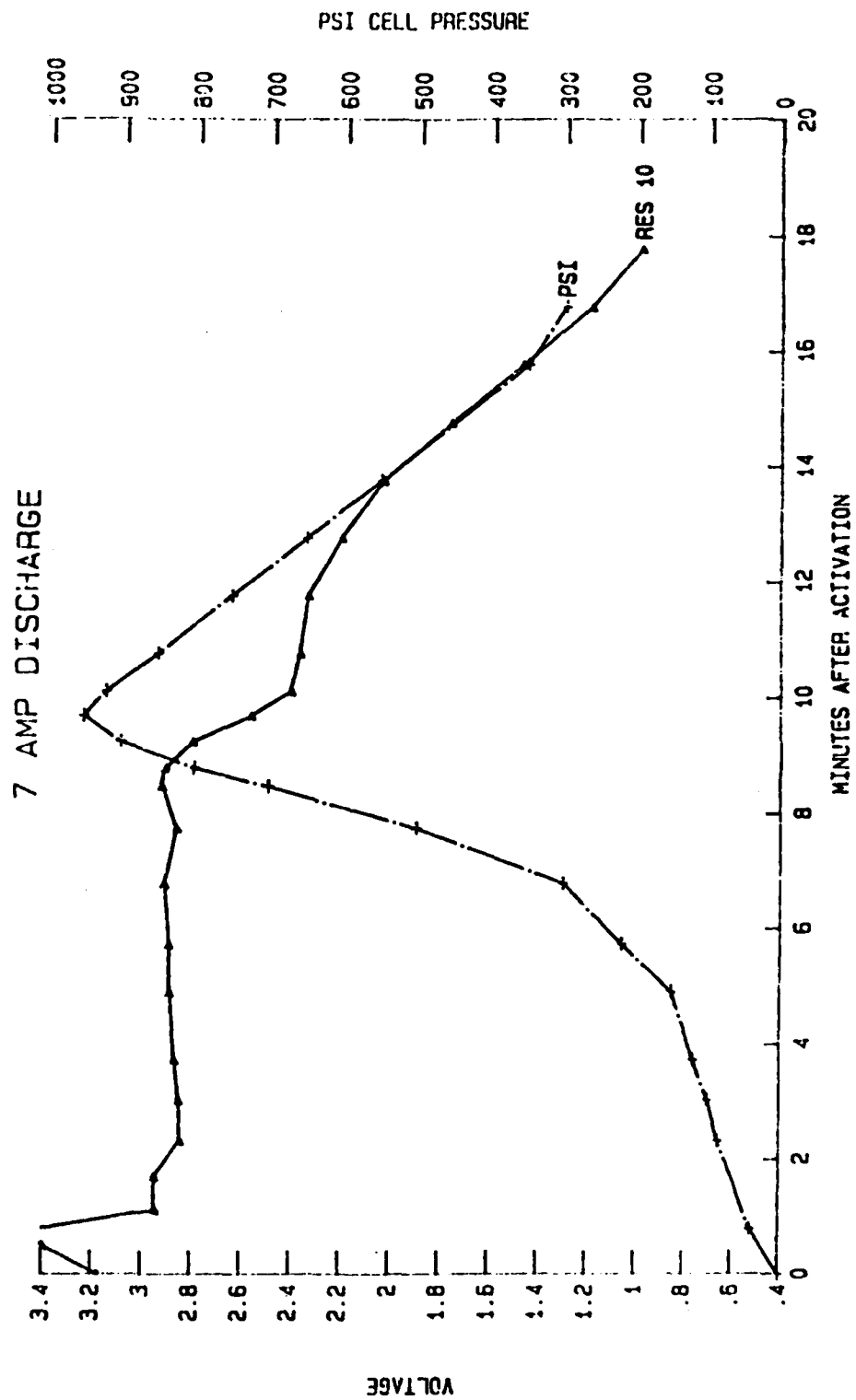


FIGURE D-22 Reserve Cell RES 10 Discharge Curves

TEMP VS TIME

RESERVE CELL 10

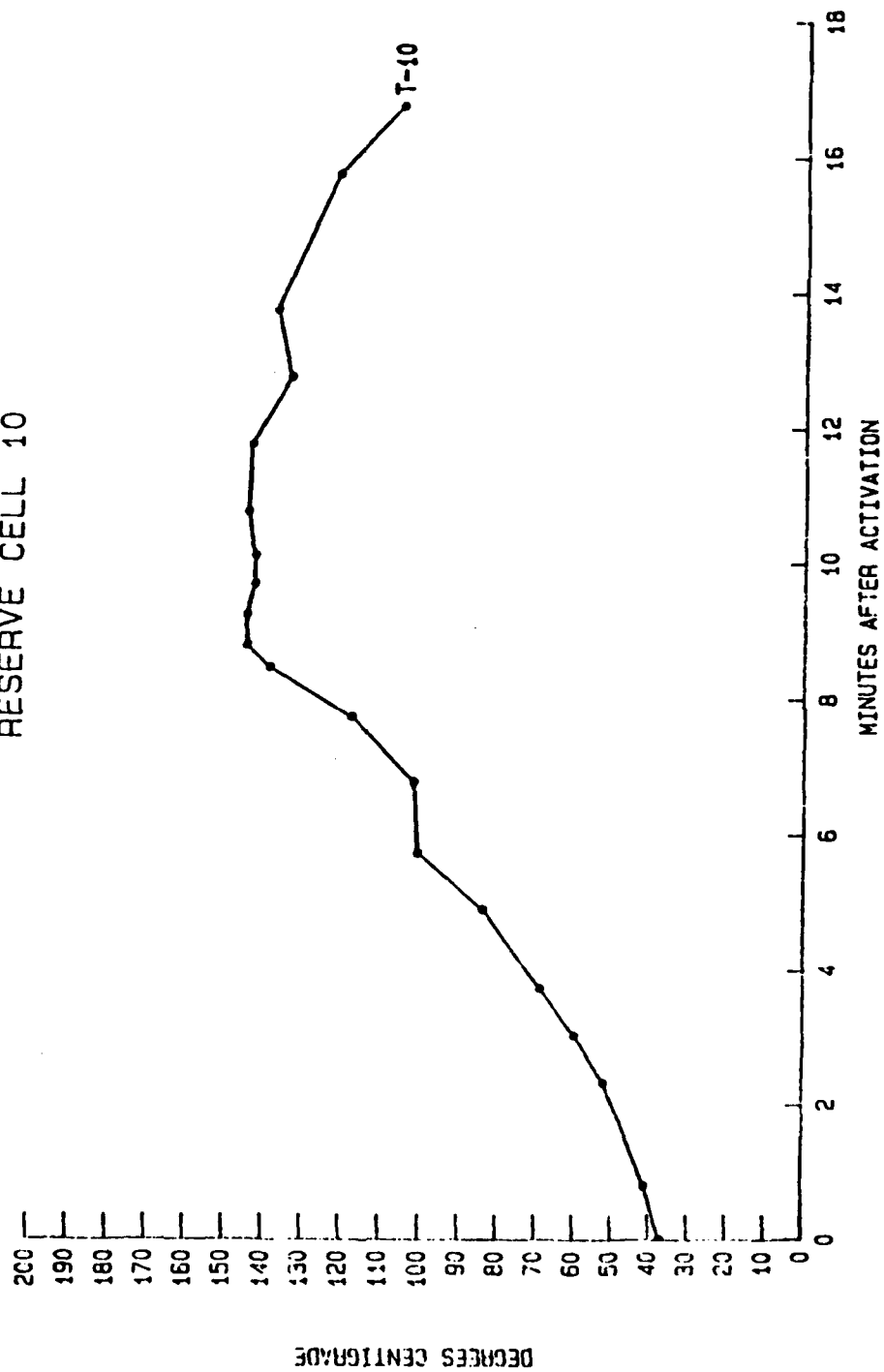


FIGURE D-23 Reserve Cell RES 10 Discharge Temperature Curve

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